THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

A FUNDAMENTAL STUDY OF POLYMER FLOCCULATION AND RETENTION AIDS

Project 3143

Report Two

A Progress Report

to

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SUMMARY

This report covers investigations of the flocculation of TiO_2 by various polyelectrolytes and the retention of TiO_2 on fibers as influenced by polymeric retention aids.

Flocculation was produced by either alum or polyethylenimine alone or by one of these in conjunction with the anionic polyelectrolyte, sodium polystyrene sulfonate. It was found that the optimum concentration for best flocculation was only weakly dependent on molecular weight and not measurably dependent on molecular weight distribution. Depending on conditions, optimum flocculation could be produced at either strongly positive or negative zeta potentials. When excess polymer was added to achieve a zero zeta potential, restabilization occurred. Only in the case of flocculation by use of alum alone was the optimum condition near zero zeta potential. These results provide strong arguments against the concept of flocculation via charge neutralization for these polymer systems. Companion adsorption measurements show that the coverage of the surface of the TiO_2 particles by polymer at maximum flocculation is small. This result and the lack of a strong dependence on molecular weight suggest that the predictions of LaMer's bridging theory are not applicable when strongly charged polymers are employed.

Retention of TiO_2 on pulp fibers was studied in conjunction with handsheet formation. For most additives the light scattered by the sheet was found to be a linear function of the amount of TiO_2 retained. Exceptions were shown to be due to preflocculation of the pigment. A correlation was found between the

percentage retention and the zeta potential of the white water with values of the latter in the range -18 to -26 millivolts corresponding to the highest retentions (50-80%). When the zeta potential is near zero (-10 to +10 millivolts), retention is moderate at about 30%. As the zeta potential is increased to still more positive values the retention decreases toward zero. The effects of the kind and amount of polymeric additive on retention and sheet properties were investigated, including the case of dual polymer addition-cationic followed by anionic polyelectrolytes. Conclusions parallel those obtained from the flocculation experiments.

INTRODUCTION

This progress report is divided into two parts. The first deals with the flocculation of TiO_2 particles by various polymer systems and the associated polymer adsorption studies. The second part covers the work on retention of TiO_2 particles in the sheet using a traditional handsheet mold for formation.

The objectives of the project are to gain a better understanding of the flocculation and retention processes at the molecular and colloidal level. With these in mind, a series of essentially monodisperse samples of sodium polystyrene sulfonate (NaPSS) over a range of molecular weights from 7×10^4 to 4×10^6 were synthesized (1). These were to be used as model flocculation and retention aids with TiO_2 dispersions. Earlier it was found that NaPSS by itself did not bring about effective flocculation. The desired effect could be produced, however, using either aluminum ion (in the form of its hydrated complexes) or polyethylenimine (PEI) as an intermediary between the negatively charged NaPSS and TiO_2. These two-component flocculation aids made possible the determination of the effect of molecular weight on the flocculation process.

The PEI/NaPSS combination was also used in the retention studies. The effectiveness of the two-step process (using a cationic polymer followed by an anionic polymer) in retention of filler has recently been shown by Britt (2). A patent on this idea was issued twelve years ago (3). The dual polymer addition as well as cationic polyelectrolytes alone were found to produce good retention.

PART I. ADSORPTION AND FLOCCULATION — TiO_2 PLUS POLYMERS

MATERIALS AND METHODS

The experiments were carried out using the fractionated TiO_2 dispersion and sodium polystyrene-sulfonate (NaPSS) fractions and commercial samples described in Progress Report One (1). In addition, some studies were made with two cationic polyelectrolytes, polyethylenimine (PEI) and chitosan. The former was a research sample (SA 1117) generously supplied by The Dow Chemical Company and has been the subject of several theses on adsorption and flocculation at the Institute (4-6). This material was prepared with no additional cross-linking agent and has a weight average molecular weight (6) of 6200. It is a highly branched polymer having primary, secondary, and tertiary amine groups in the ratio 1:2:1 with the tertiary groups providing the branching points. Chitosan has a chemical structure identical to cellulose except that an amino group replaces the hydroxyl group at C-2. It is soluble in water only at a pH below about 6.5 and has a moderate molecular weight of several hundred thousands. The sample was furnished by Food, Chemical, and Research Laboratories, Inc. (Seattle, Wash.). Distilled deionized water was used throughout these studies to eliminate the day-to-day variability in the impurity level found in tap water.

Adsorption measurements were performed at a level of 7400 ppm TiO_2 which corresponds (1) to a surface area of 3.76 m^2 in a sample of 40-ml volume. The pH of both the TiO_2 dispersion and the polymer solution to be added was separately adjusted to the same value. The two components were then mixed using a magnetic stirrer at moderate speed for five minutes. Preliminary experiments showed this mixing time to be sufficient for essentially complete adsorption equilibrium. In those cases where a second polymer (of opposite charge) was added

subsequent to the adsorption of the first, a second mixing time of five minutes was allowed. Following the mixing (adsorption) step the sample was centrifuged to remove the suspended TiO_2 in a Sorvall Superspeed RC2-B centrifuge. A sample of the clear supernatant solution was carefully removed by pipet and analyzed for the amount of polymer remaining unadsorbed by UV spectrophotometry.

The analysis for NaPSS was carried out at a wavelength of 225 nm as previously described (1). The amount of PEI remaining unadsorbed was determined according to the method of Perrine and Landis (7) as modified by Kindler (4). This procedure is based on the formation of a complex between the amine groups on the PEI and cupric ions which are added as a reagent. The complex has an absorption maximum at 269 nm. Kindler's modification consists of adding one milliliter of color reagent solution containing 0.01M cupric acetate and 0.01M hydrochloric acid to 5 ml of the solution containing PEI. A series of known concentrations of PEI were prepared, reacted with the reagent, and measured on the Beckman DU spectrophotometer. The resulting plot of absorbance against polymer concentration is linear up to at least 75 ppm PEI.

Flocculation experiments were carried out in a similar manner to those for determining adsorption. A TiO_2 dispersion with a final concentration of 1000 ppm was mixed using a magnetic stirrer with one or more polymers after adjusting the pH. A mixing time of five minutes for each polymer added was used to ensure maximum interaction. Then the 15-ml sample was transferred to a centrifuge tube with a conical lower section and centrifuged at 2000 rpm for one minute. This rather mild centrifugation, insufficient to cause unflocced and partially flocced TiO_2 to sediment, did remove well-flocced TiO_2 from the suspension and made possible transmittance measurements unperturbed by concentration changes due to settling over the time scale of the measurement — a few minutes. A 5-ml sample of the

supernatant was withdrawn from the centrifuge tube by pipet and transferred to a clean test tube with a diameter of 1.6 cm. The amount of light able to pass through this tube was determined using an instrument especially constructed for this purpose. The tube is illuminated by a white light powered by a stable voltage source. The light able to pass through the suspension is detected by a silicon photocell whose output is connected to a sensitive microammeter. On this instrument the transmittance of a 1000 ppm TiO_2 dispersion (with no additives) either before or after the centrifuge step is about 3 microamperes. At the other end of the scale the transmittance of a sample of distilled water or of the supernatant obtained from centrifuging a well-flocced suspension is about 160 microamperes. A calibration curve of transmittance (T) against concentration of TiO_2 is shown in Fig. 1. The sensitivity is sufficient to detect less than one ppm TiO_2 remaining unflocculated. Considerable difficulty was experienced with sticking of the flocculated TiO_2 to the upper portions of the walls of the centrifuge tube. Some of this material would then become resuspended upon withdrawal of the 5-ml sample and lead to irreproducible results. This problem was overcome by treating the centrifuge tubes (and other glass apparatus where necessary) with Dri-Film SC-87 siliconizing fluid (PCR, Inc., Gainesville, Fla.). The treatment produces a hydrophobic surface which prevents the TiO_2 from sticking.

The electrophoretic mobility of several of the suspensions was determined using a Zeta-Meter (Zeta-Meter Inc., New York, N.Y.). This is a microelectrophoresis apparatus whose sample cell is cylindrical in shape and has a cross-sectional diameter of about 4 mm. The mobilities are converted to zeta potentials (ζ) using the Helmholtz-Smoluchowski equation (8):

$$\zeta = 4\pi\mu\eta/\varepsilon E \qquad (1)$$

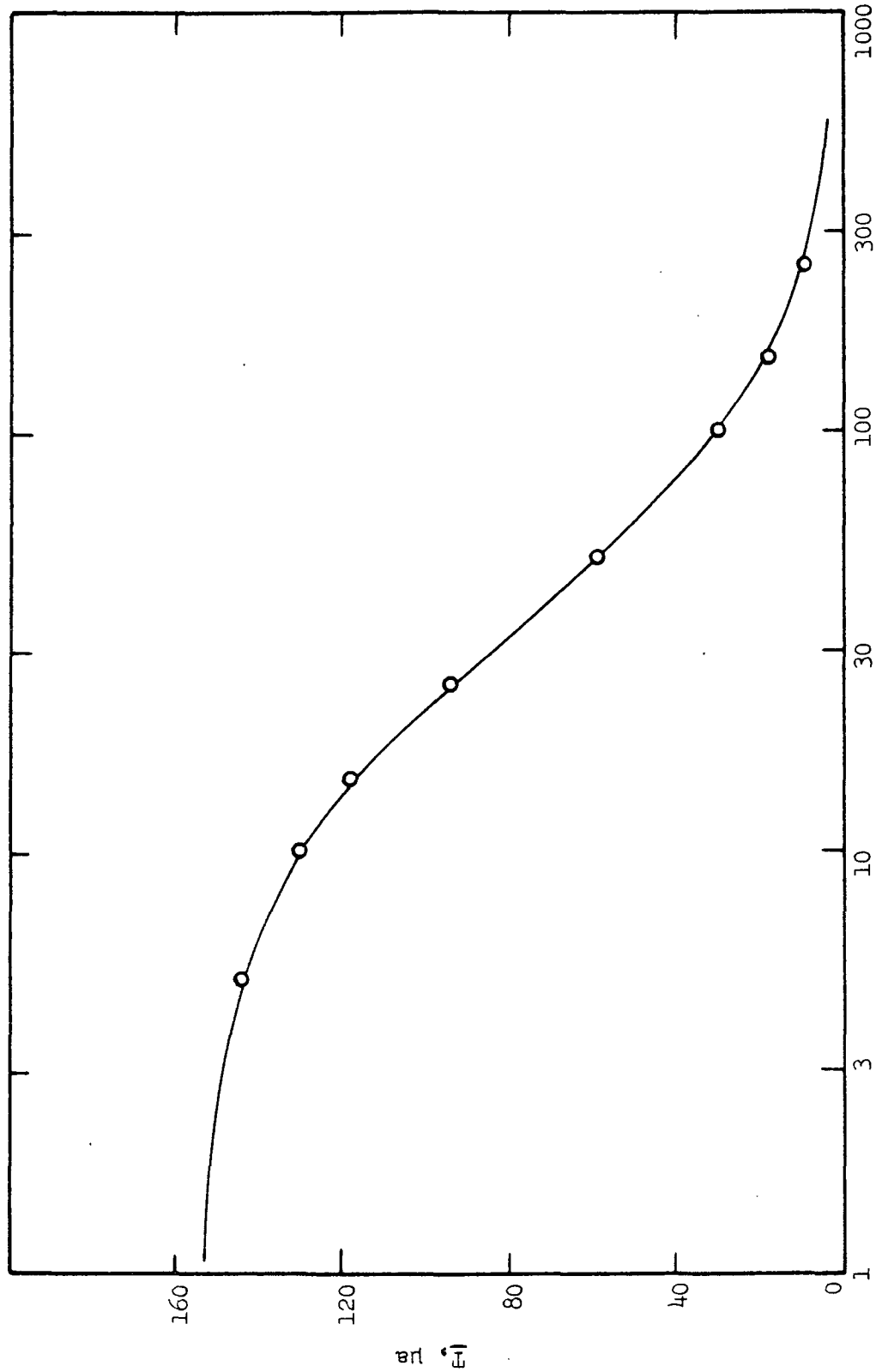


Figure 1. Semilogarithmic Plot of Transmittance Against Concentration of TiO_2 Suspension

Here μ is the electrophoretic mobility of the particles, η and ε are the viscosity and dielectric constant, respectively, of the suspending fluid, and E is the electric field strength applied to the suspension. The relation assumes that the particles are spherical and that the thickness of the electrical double layer is small compared to the size of the particle. These are reasonable assumptions for the present system; therefore the results will be discussed in terms of the zeta potentials. Because at concentrations of TiO_2 greater than about 5 ppm, individual particles are extremely difficult if not impossible to track when viewed through the microscope, the samples are first centrifuged for 15-30 minutes at 3700 rpm in the International centrifuge, Model V. Supernatant fluid is then withdrawn for use in the electrophoresis cell. If centrifuging has removed virtually all the TiO_2 particles (i.e., in the cases of good flocculation), a drop of the original suspension is mixed with the supernatant fluid. The centrifuging procedure ensures that the diluted suspension will have the same ionic strength, pH, and composition of soluble materials as did the original concentrated suspension.

RESULTS AND CONCLUSIONS

ADSORPTION

The effect of pH on the adsorption behavior of PEI on TiO_2 was studied at pH levels of 5, 7, and 9. The adsorption isotherms for pH of 5 and of 9 are shown in Fig. 2. Here the amount of PEI adsorbed, C^*, on 7400 mg/liter TiO_2 is plotted against the amount of PEI remaining unadsorbed, C_e. The amount adsorbed C^* is obtained by difference between the known initial concentration C_i and the measured equilibrium concentration C_e. At higher concentrations the amount adsorbed tends toward a limiting value. This kind of adsorption behavior is said to be of the Langmuir type and is commonly found for the adsorption of many polymers on different solid substrates. Silberberg (9) has shown that the characteristic shape of the isotherm is the common product of several different models of polymer adsorption. The only requirements are that the adsorption sites be spread homogeneously over the surface and that the adsorbed polymer segments interact only with the surface adsorption sites and not with each other. There is no clear picture of the physical situation prevailing under conditions of surface saturation, i.e., the plateau region in Fig. 2. The degree of interpenetration of segments of one adsorbed polymer molecule with those of its neighbors and the thickness of the adsorbed polymer "layer" remain unknown.

If the Langmuir equation is rearranged (Appendix I), the experimental quantities in Fig. 2 can be replotted to yield a linear plot whose slope and intercept can be identified with the two constants of the equation. This kind of plot is shown in Fig. 3. The constants derived are the maximum amount of polymer that can be adsorbed, C^*_M, and the Langmuir affinity constant, K, which is a measure of the strength of the interaction between the adsorbate and adsorbent.

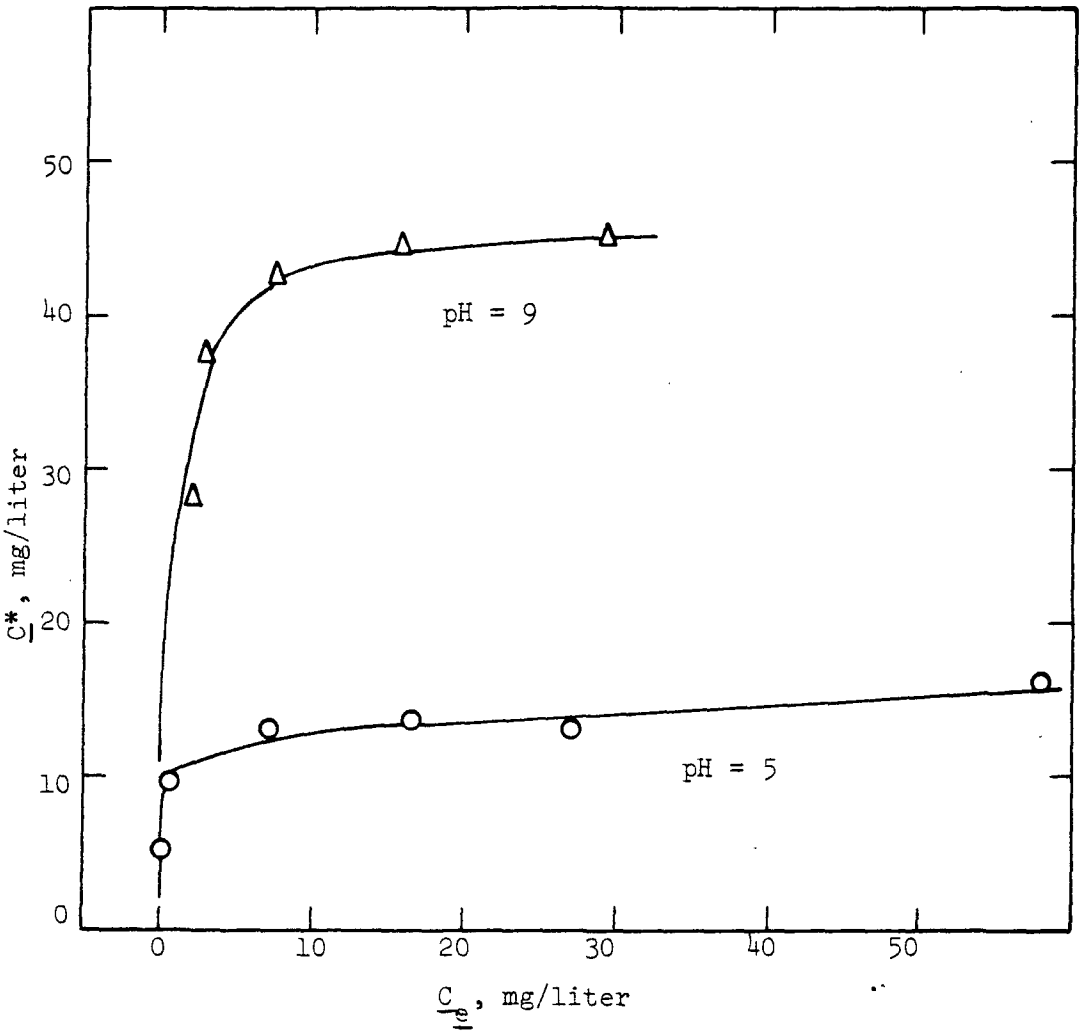


Figure 2. Amount of PEI Adsorbed on 7400 mg/liter TiO_2 Plotted Against Concentration of PEI Remaining Unadsorbed at the Indicated pH

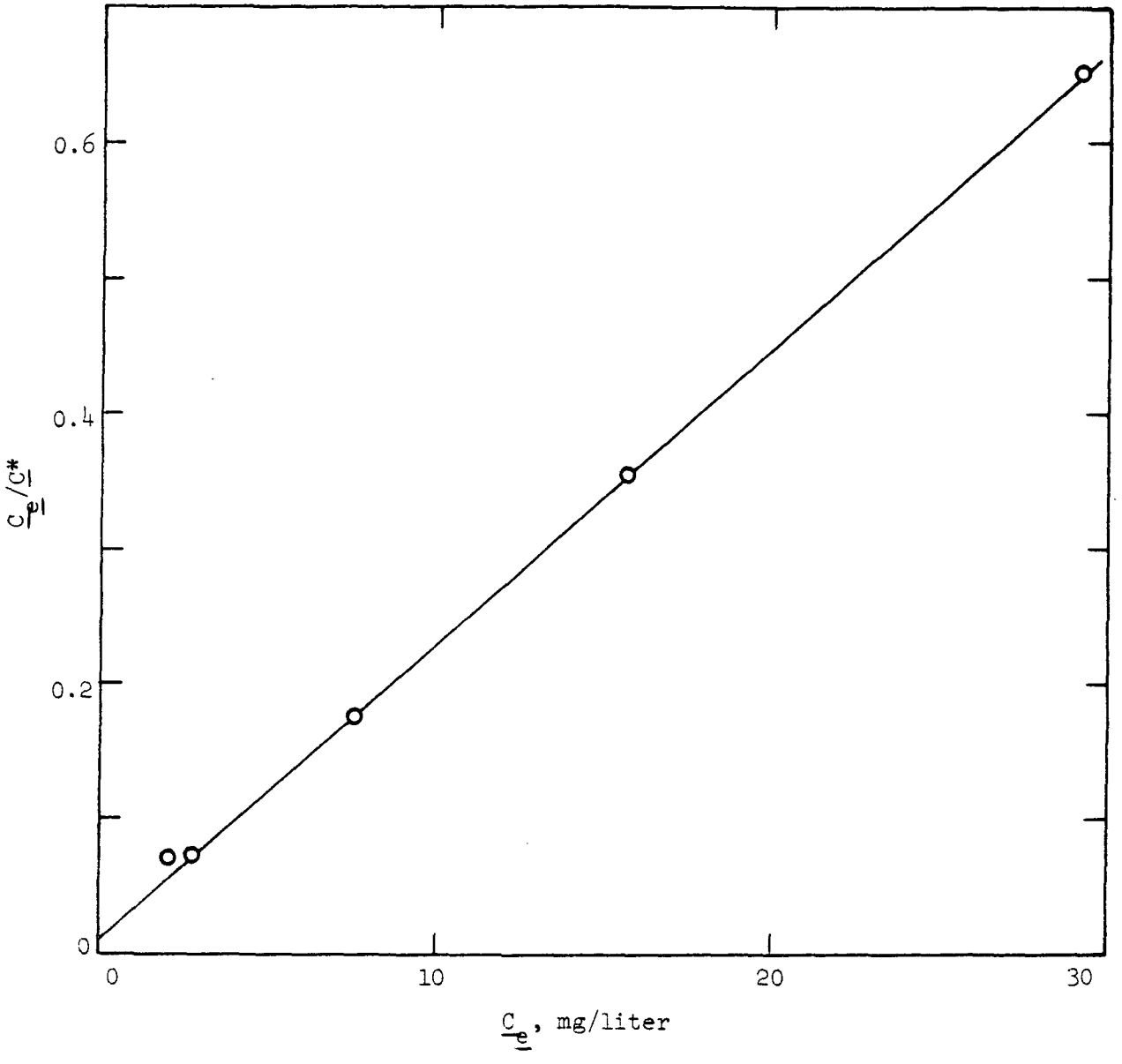


Figure 3. Plot According to the Linearized Form of the Langmuir Equation (4) for PEI Adsorbed on 7400 mg/liter TiO_2 at pH 9

The values of these constants for the different pH conditions are given in Table I. It should also be noted that C_M^* is directly proportional to the amount of TiO_2 present but that K is independent of this amount. Examples are given in Appendix I of the calculation of various quantities of interest for an arbitrary initial amount of TiO_2. The data in Table I are plotted in Fig. 4 showing the variation of the maximum amount of polymer adsorbed, C_M^*, with pH. The decreasing amounts of PEI adsorbed as the pH is lowered is a product of several factors. There is some evidence from zeta potential measurements (see below) that the surface charge density of the TiO_2 particles including their polyphosphate stabilizer decreases slightly with decreasing pH leading to fewer sites for electrostatic adsorption. Of probably greater importance are changes in the PEI molecules. At pH levels of 9, 7, and 5, the degrees of protonation of the PEI amine groups are 0.10, 0.34, and 0.55, respectively (6). The increasing electrostatic repulsion at the lower pH levels between the protonated amine groups on PEI molecules already adsorbed and those approaching the surface leads to a wider spacing between adsorbed polymer molecules. Also producing an increased spacing is the expansion in size (6) of the PEI molecules by about 25% as the pH is lowered from 9 to 5. This effect is caused by intramolecular repulsion of protonated amine groups. These same factors influence the amount of PEI necessary for flocculation, as will be discussed below.

TABLE I

LANGMUIR PARAMETERS FOR THE ADSORPTION OF PEI ON TiO_2 AT A CONCENTRATION OF 7.4 g/liter AND VARIOUS pH

pH	C_M^*, mg/liter	K, liter/mg
5.0	15.6	1.6
7.0	27.0	∿2.0
9.0	45.8	2.0

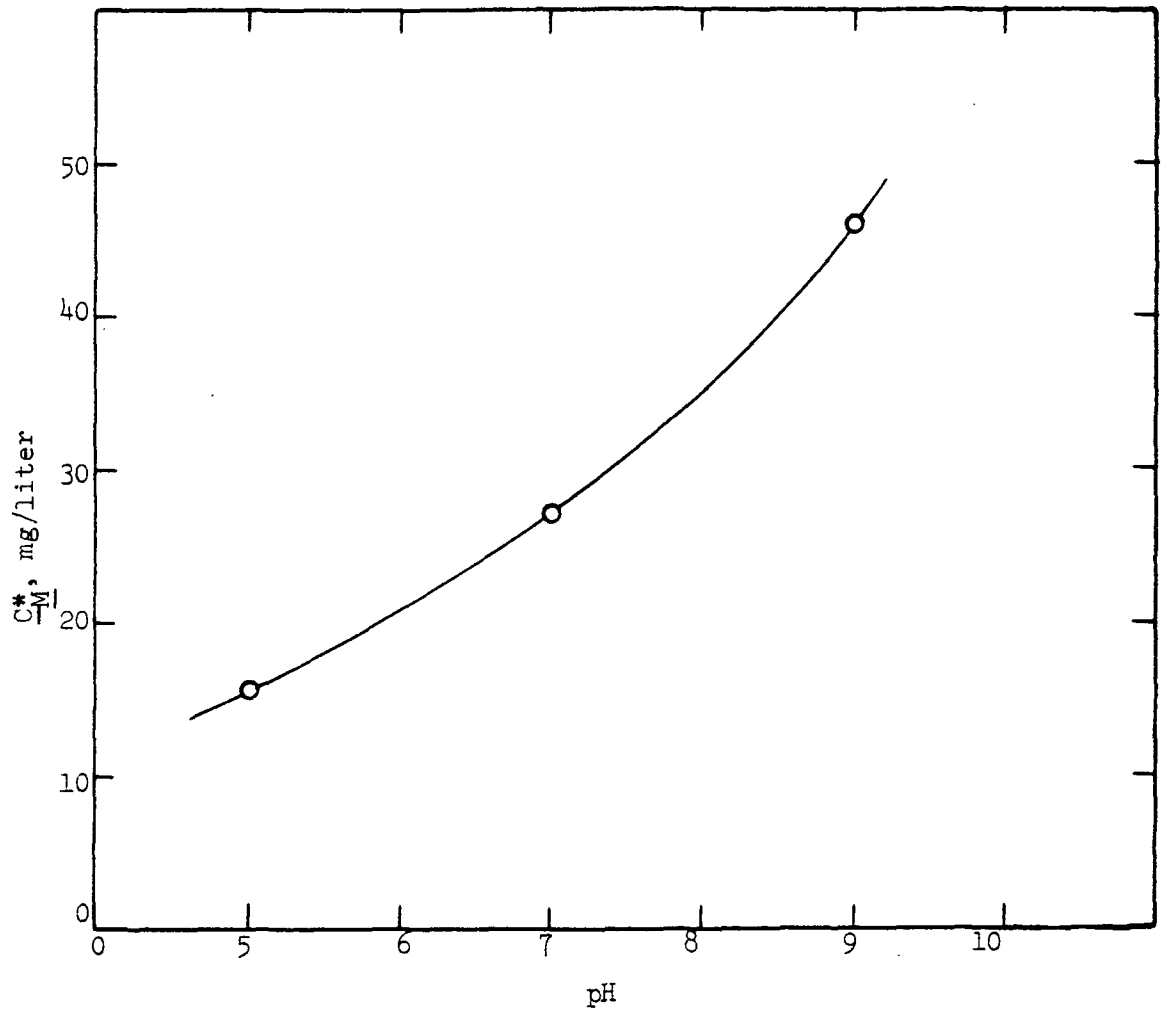


Figure 4. Dependence of the Maximum Amount of PEI Adsorbed on 7400 mg/liter TiO_2 on pH

It might be noted that the values of the affinity constant $\underline{K}$ found here are about a factor of 10 or more larger than the values found for the adsorption of PEI on viscose rayon (4) and on porous (5) and nonporous (6) silica. This indicates a much stronger adsorption in the present case. Stated differently, to reach near maximum adsorption $\underline{C}_M^*$ (or any fraction of $\underline{C}_M^*$) a much greater excess of polymer $\underline{C}_e$ is necessary for the other three materials as compared with that for TiO_2.

Since a number of flocculation experiments (and, subsequently, retention studies) involved the sequential treatment of the TiO_2 by first PEI and then NaPSS, it was of interest to determine whether NaPSS adsorption in this instance followed a Langmuir-type adsorption isotherm. A series of experiments were conducted in which 7400 mg/liter TiO_2 were mixed with 30 mg/liter PEI and then with either 1, 2, 5, 7, 10, or 20 mg/liter V-500. The concentrations given are those in the final volume which had a pH of 9. Calculations based on the Langmuir constants for the PEI-TiO_2 system (Table I) indicate that over half the TiO_2 surface is covered by positively charged PEI molecules. The amount of NaPSS (V-500) remaining unadsorbed was determined and the results are plotted in Fig. 5. The similarity in shape of this curve to those of Fig. 2 is obvious. A plot based on Langmuir's equation (as in Fig. 3) was linear and yielded values of $\underline{C}_M^*$ and $\underline{K}$ of 19.2 mg/liter and 1.3 liter/mg, respectively. Apparently, the adsorption of the NaPSS onto the PEI-TiO_2 surface proceeds in an analogous manner to the adsorption of PEI on TiO_2. That this is intuitively reasonable may be surmised from a consideration of the size of the entities involved. The average size of a TiO_2 particle is 1520 A in diameter (1), that of the PEI molecules is about 56 A in diameter (6). Assuming little change in size of the polymer molecule upon adsorption, a monolayer of PEI would add only about 7% to the diameter of the TiO_2 particle. An approaching

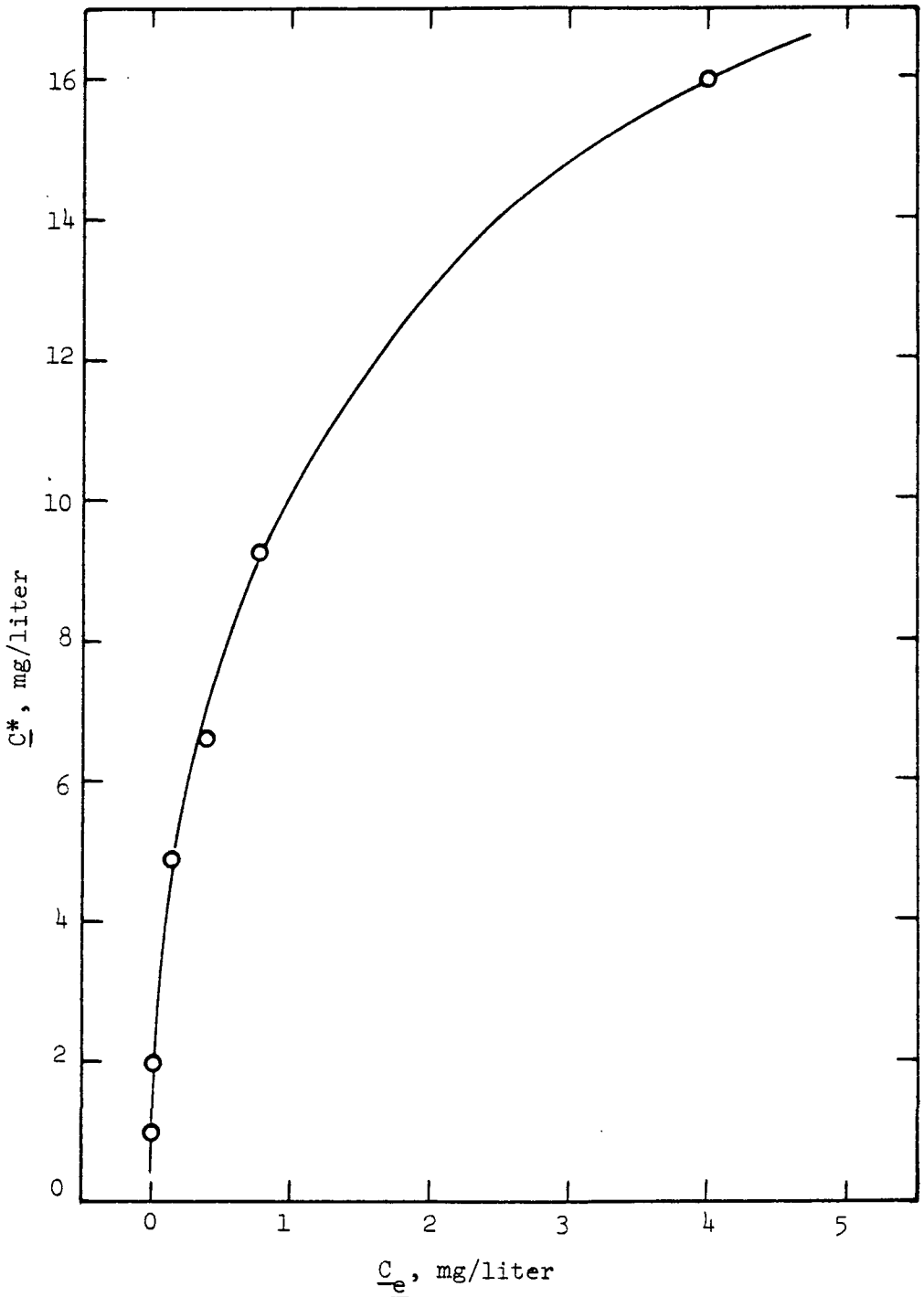


Figure 5. Amount of NaPSS (V-500) Adsorbed at pH 9 on 7400 mg/liter TiO_2 (Pretreated with 30 mg/liter PEI) Plotted Against Concentration of NaPSS Remaining Unadsorbed

NaPSS molecule with a molecular weight of 5×10^5 has a radius of gyration in excess of 600 A (10). It "sees" a fairly smooth surface with positively charged sites with which to interact. The situation is not very different from that of the NaPSS molecule interacting with a TiO_2 surface modified by adsorbed, positively-charged, hydrated aluminum complexes as will be evident in the flocculation results below.

FLOCCULATION OF TiO_2

A number of different flocculation aids were used. In the following discussion the progression will be from simpler to more complex systems.

Alum Only, pH About 4.5

Alum alone can be used to flocculate TiO_2. This is a well-known fact in the paper industry and is used to good advantage in the retention of TiO_2 in paper. The results in Fig. 6 show the transmittance of the supernatant fluid of the flocculated system as a function of the amount of alum. Only a very limited range of concentrations, 4-7 mg/liter alum, produces effective flocculation with about 5 mg/liter, or 0.5% based on the TiO_2, being the optimum. A negative slope of the transmittance-concentration curve is indicative of restabilization. Also shown in Fig. 6 is the zeta potential, ζ, for the same systems. Maximum flocculation occurs at ζ = -10 millivolts (mv) with restabilization of the colloid obtaining at higher concentrations of alum as the particles become positively charged. These findings are in agreement with numerous studies (11-13) of the flocculation of negatively charged colloids by multivalent cations.

Alum Plus NaPSS, pH = 4.5

The flocculation aids in this system are added to the TiO_2 in two steps. First, alum is added to a TiO_2 dispersion (1000 mg/liter) to give a concentration of

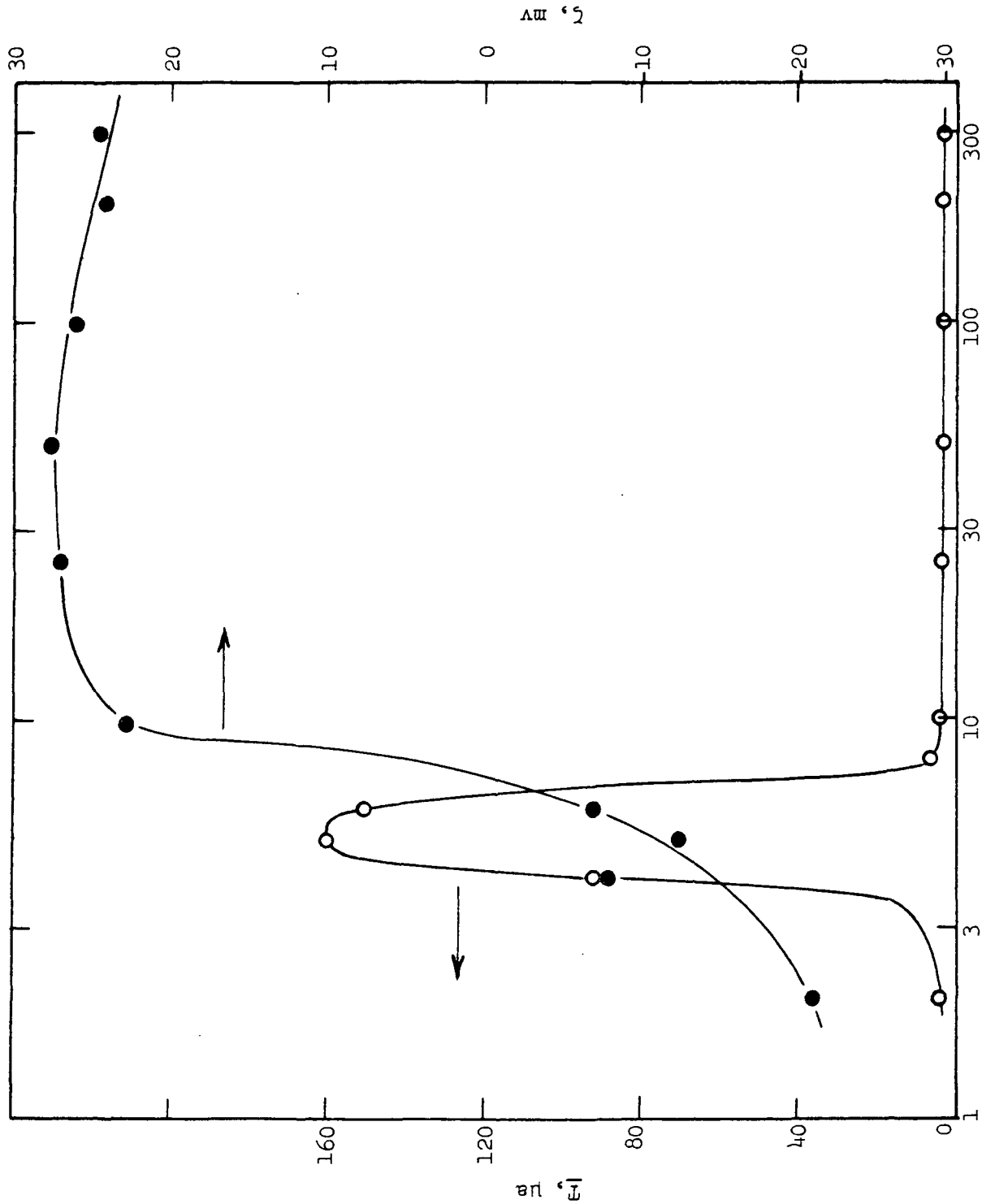


Figure 6. Flocculation of 1000 mg/liter TiO_2 Dispersion. Semilogarithmic Plot of Transmittance and Zeta Potential Against Alum Concentration

10 mg/liter. In much waste water treatment, Al(III) or Fe(III) is added as a sensitizer to be followed by an anionic polyelectrolyte. In the present work alum addition level is relatively higher. According to the zeta potential and transmittance results in Fig. 6 the TiO_2 particles have been restabilized with a positive surface charge. At this point a given concentration of NaPSS is mixed into the dispersion and the degree of flocculation (transmittance) and zeta potential are determined. The transmittance data for three different samples of NaPSS are presented in Fig. 7. These are the samples with highest ($\underline{M} \tilde{=} 4 \times 10^6$) and lowest ($\underline{M} \tilde{=} 7 \times 10^4$) molecular weight and a 50:50 blend of the two. In contrast to the predictions of the "bridging" theory of LaMer and Healy (14), the effect of a 50-fold increase in molecular weight is seen to be small. For effective flocculation the concentration range here is somewhat broader and the median concentration is lower for the high molecular weight polymer compared with the low. These results are in accordance with the recent report of Gregory (15), who studied the flocculation of negative particles by cationic polyelectrolytes. He, too, found only a slight dependence of optimum concentration of flocculant on molecular weight but noted the increasing breadth of his flocculation rate curves with increasing molecular weight. Gregory (15) suggests that this behavior may be explained in terms of the uneven charge density on a colloid particle partially covered by polymer. There is as yet no quantitative theory to be tested.

The results for the blend are approximately midway between those for the two components. The flocculation produced is obviously not just an additive function of the amounts of each since the low molecular weight polymer is able to enhance the action of the S-3960 at concentrations where it (S-73) would be totally ineffective by itself. This behavior may also be explained in terms of the uneven charge distribution and the ability of the smaller molecule to diffuse

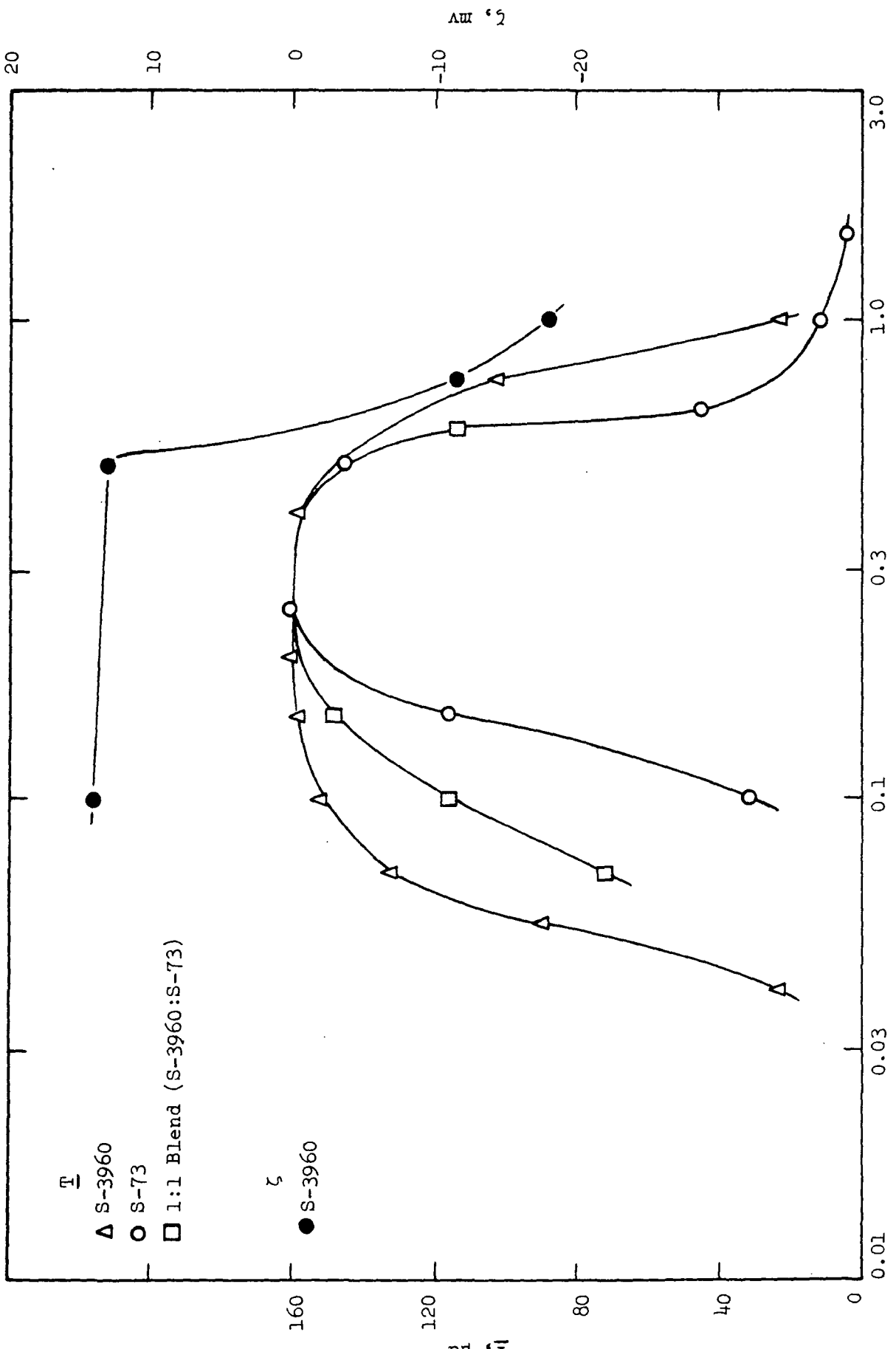


Figure 7. Flocculation of 1000 mg/liter TiO_2 Dispersion Treated with 10 mg/liter Alum. Semi-logarithmic Plot of Transmittance and Zeta Potential Against Concentration of the Indicated Samples of NaPSS

quickly to the particles, partially neutralize the latter's surface charge, and thereby to promote bridging by the larger molecules.

The zeta potentials measured for S-3960 are also shown in Fig. 7. Here the charge on the particles rendered positive by the adsorption of aluminum ions rapidly becomes negative as an excess of NaPSS is adsorbed and restabilization occurs. It is to be noted that optimum flocculation takes place at ζ = +13 mv or somehat higher than is usually predicted.

PEI Only, pH = 5

These experiments show the effect of flocculation of the negative TiO_2 particles by a relatively low molecular weight cationic polyelectrolyte. The results are plotted in Fig. 8. The concentration range over which the flocculant is effective is considerably narrower than that for the NaPSS systems discussed above. This may reflect the lower molecular weight of the PEI compared with the NaPSS samples or a difference in mode of action. Polyethylenimine is a branched, rather compact molecule with a high charge density (charge/volume) while NaPSS is a linear, rather extended chain with a considerably lower charge density. These differences are further magnified by the results of the zeta potential measurements in Fig. 8. Optimum flocculation occurs at a zeta potential of -30 mv! Restabilization is complete before the concentration of PEI necessary to produce a zero zeta potential is reached. Evidently, the PEI adsorbs on the TiO_2 to produce local areas of high charge density which are quite effective in producing flocculation but which increase the zeta potential only slightly.

The relative concentration of PEI on the surface can be calculated from a knowledge of the Langmuir constants as illustrated in Appendix I. At PEI concentrations of 0.1, 0.25, and 0.5 mg/liter, corresponding to unflocculated,

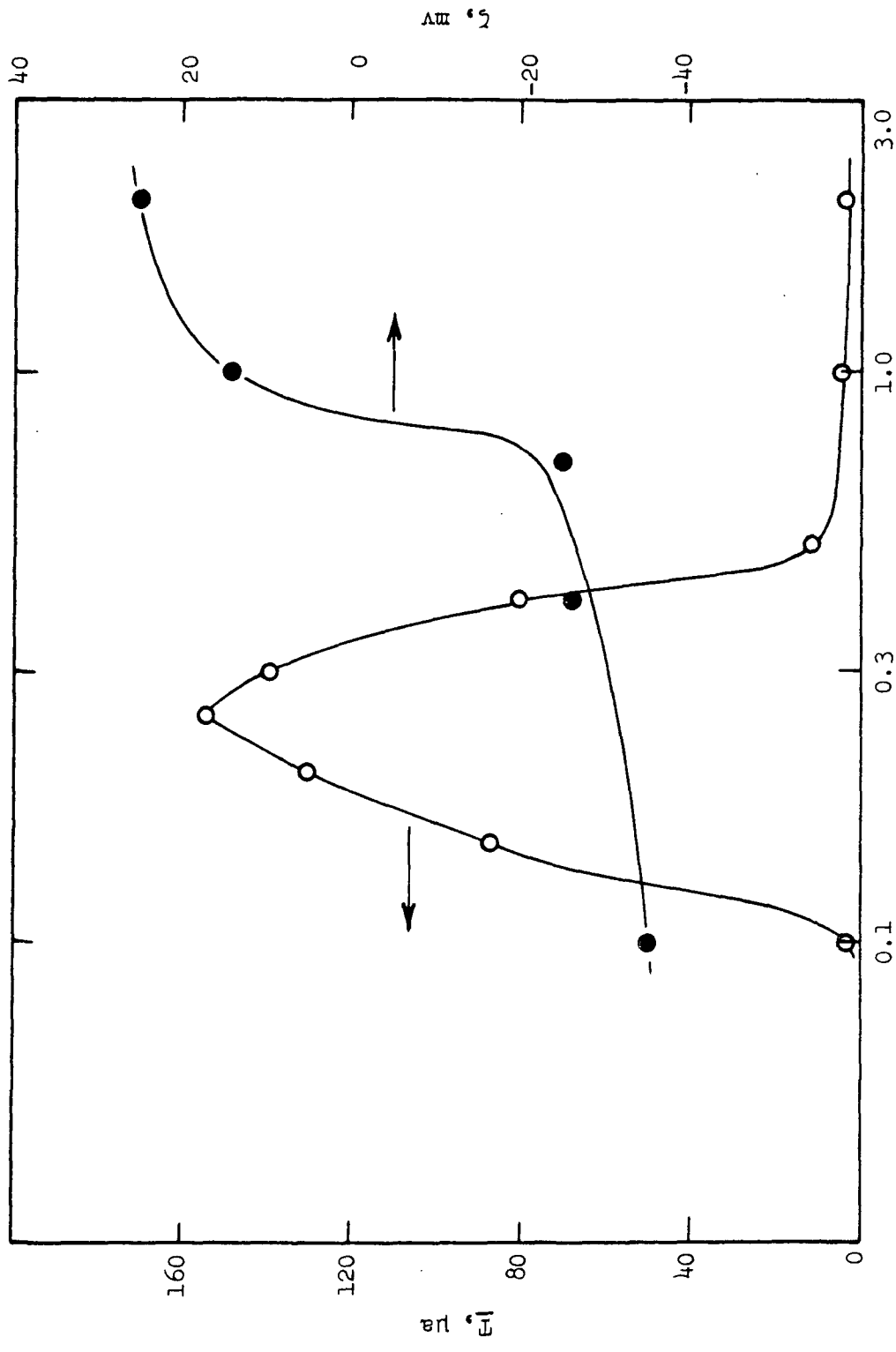


Figure 8. Flocculation of 1000 mg/liter TiO_2 Dispersion. Semilogarithmic Plot of Transmittance and Zeta Potential Against Concentration of PEI

optimally flocculated, and restabilized states, respectively, the fractional areas of the surface covered, θ, are 3.7, 9.0, and 17.5%, respectively. These results bear out the statements made in the preceding paragraph and are in disagreement with the predictions of LaMer's bridging theory. The latter predicts (14) optimum flocculation to take place at a θ of 50%. The initial concentration of PEI necessary to produce coverage of half the surface (θ = 50%) can be calculated by Equation (9) in Appendix I. The value is 1.7 mg/liter. At this concentration, according to Fig. 8, the colloid is completely restabilized and the zeta potential is strongly positive showing the effect of the high charge density of the PEI. Apparently neither charge neutralization, which would have optimum flocculation at zero zeta potential, or "bridging" as described by LaMer's theory, can explain the results found here.

Chitosan, pH = 5

The range of concentrations over which flocculation occurs for this linear cationic polymer is somewhat broader than that for PEI (Fig. 8) and closely resembles that for S-73 in Fig. 7. The higher concentration for optimum flocculation (0.5 mg/liter), compared with those for S-73 and PEI (0.3 and 0.25, respectively) probably reflects a weaker adsorption, so that at a given concentration a smaller fraction of chitosan is adsorbed compared with the other polymers.

NaPSS Alone, pH = 5

No flocculation could be produced by use of this polymer alone. An adsorption experiment starting with an initial concentration of 15.3 mg/liter of NaPSS on 7400 mg/liter TiO_2 at a pH of 5 produced only 0.7 mg/liter NaPSS adsorbed. This amount of polymer, however, increased the zeta potential from -35 mv with no polymer to -50 mv, thereby decreasing the likelihood of flocculation.

PEI Plus NaPSS, pH = 7.5

In order to achieve flocculation with NaPSS on the alkaline side, PEI was adsorbed first to provide positively charged sites for interaction with the polyanion. Preliminary experiments showed that an initial PEI concentration of 3 mg/liter on 1000 mg/liter TiO_2 was sufficient to provide complete re-stabilization. (A PEI concentration of 0.7 mg/liter provides optimum flocculation at this pH.) Calculations based on the Langmuir equation revealed a fractional surface coverage of 56% at this concentration (3 mg/liter).

Both sets of NaPSS polymers were used as flocculants. The V series are commercial materials having a broad molecular weight distribution while the S series are characterized by a narrow molecular weight distribution (1). In contrast to the results above where alum plus NaPSS was used, the range of concentrations over which effective flocculation was produced was relatively narrow — about like S-73 in Fig. 7 — and was independent of molecular weight and molecular weight distribution. There was a slight dependence on molecular weight of the optimum concentration, defined here as the median of the transmittance/concentration curve near the maximum. The optimum concentration is plotted against molecular weight in Fig. 9. Although separate curves have been drawn for the two series, a single curve would equally well represent the data within the error of determining the median of the transmittance curves. The higher molecular weight polymers are slightly more efficient in promoting flocculation than the low molecular weight species which suggests that something more than mere charge neutralization is occurring. Again the lack of a strong dependence on molecular weight argues against the "bridging" mechanism at least as described by the LaMer theory.

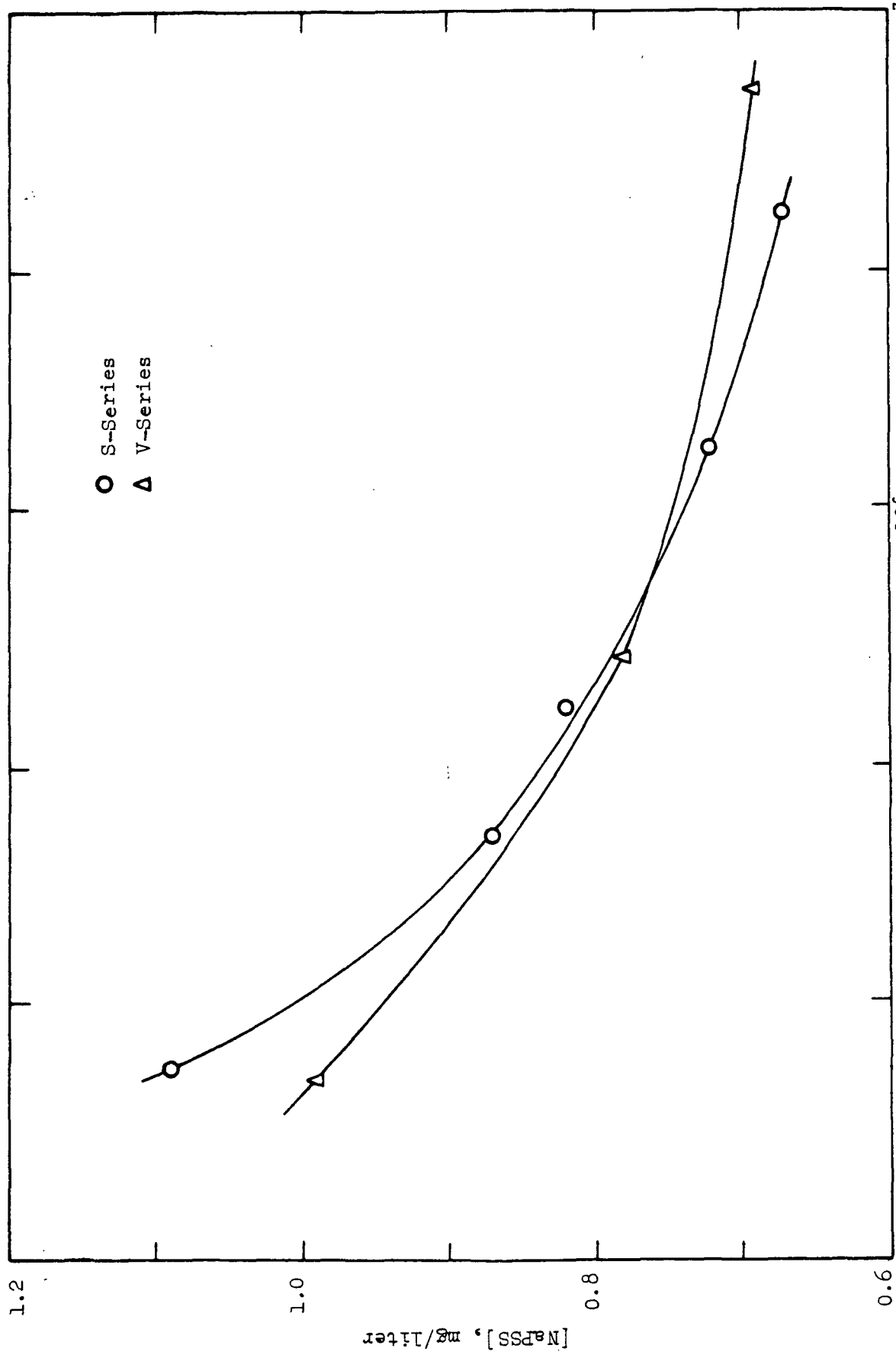


Figure 9. Optimum Concentration of NaPSS for Maximum Flocculation of 1000 mg/liter TiO_2 Treated with 3 mg/liter PEI at pH 7.5 Plotted Against the Logarithm of Molecular Weight of NaPSS

On the basis of the results obtained under a variety of conditions and with differing dependencies on molecular weight and zeta potential, it must be concluded that at least two factors influence the flocculation process. Neither charge neutralization nor bridging as presently understood can explain the observed behavior, whether used separately or in conjunction. Further work will be required to elucidate the factors critical to the flocculation process.

PART II. RETENTION OF TiO_2 ON HANDSHEETS

MATERIALS AND METHODS

The preparation of the bleached softwood kraft pulp was described in Progress Report One (1). The TiO_2 and polymers used were also described in that report and in Part I of the present report. In addition, because of the large quantitites used in handsheet formation, a commercial sample of polyethylenimine produced by The Dow Chemical Company, Tydex 12, replaced the research sample, SA-1117, in a number of the experiments. The molecular weight and degree of cross-linking, if any, of the Tydex is not known. As will be seen below, the results produced by it at a given level of addition were very similar to those at the same concentration of the research sample. Although both samples undoubtedly have nearly identical chemical structures, they will be differentiated by the shorthand names PEI and Tydex. Another linear cationic polyelectrolyte investigated was Reten 300, a commercial product of Hercules, Inc. This material is described by the manufacturer as being a highly functional, medium molecular weight, cationic polymer.

The handsheets were all prepared in a standard manner. Deionized water was used throughout the formation. Forty grams of pulp (o.d.) were dispersed in a British disintegrator for 300 counts at 2% consistency. The pulp slurry was diluted to 1-1/2% consistency, the TiO_2 and polymer(s) were added, and the pH was adjusted to 5.0 $\pm$ 0.1 with H_2SO_4 while mixing vigorously with a Lightnin' stirrer. Total mixing time after the additions was 5 minutes at this consistency. The furnish was then diluted to 1/2% consistency and was kept stirring slowly during sheet formation. The handsheets were formed on a Noble & Wood sheet mold using a 100-mesh wire. Approximately 5-1/2 liters of deionized water was admitted

to the deckle box and adjusted to a pH of 5 with H_2SO_4. Then 500 ml of the 1/2% consistency slurry was added, the perforated mixer was plunged up and down several times and removed slowly to prevent uneven formation, and the drain was opened. The sheet was couched off the wire with a blotter and was pressed for 5 min at 50 psi between blotters. It was then dried on a steam drum for 7 min at 220°F. Eight 2.5-g sheets constituting a "set" were formed from each 40-g batch of pulp. About 500 ml of the initial portion of white water from the first sheet of each set was caught and retained for subsequent measurement of the zeta potential.

The amount of TiO_2 added to the pulp was kept constant from set-to-set at 5% based on the o.d. pulp or 2 g. It was added in the form of a 7.4% slurry or partially diluted with a polymer solution as indicated below. Polymer retention aids could be added to the furnish at several points. For the cationic polyelectrolytes the procedure, unless otherwise noted, was to mix the requisite amount of polymer (predissolved as a 0.5% solution) with the TiO_2 slurry for 5 min. This mixture was then added to the 1-1/2% consistency pulp and mixed for 5 min before dilution and sheet formation. When NaPSS was used in addition to PEI or Tydex, the procedure was as follows. The PEI or Tydex was mixed with the TiO_2 and added to the pulp slurry as above. It was stirred for 2-1/2 min at which time the desired amount of NaPSS in the form of a 0.5% solution was added to the furnish. The mixing was continued for another 2-1/2 min followed by dilution and sheet formation as usual. Another mode of addition of polymer was directly to the furnish in the deckle box followed by mixing with the perforated plunger and sheet formation. Here the contact time of the polymer with the pulp and TiO_2 was short — under 30 sec.

The zeta potential of the fines and TiO_2 in the white water was measured with the Zeta-Meter as described in Part I. It was found necessary to deaerate the

white water prior to introduction into the sample cell of the Zeta-Meter to prevent bubble formation in the cell which would lead to spurious results. The deaeration was accomplished by evacuation for 1/2-hour while stirring. The zeta potential measurements were generally made within an hour of the time at which the white water sample was taken. Studies showed that the values obtained did not change with time over a period of 24 hours. For most samples both unflocculated TiO_2 particles and fines partially covered with TiO_2 were observed. The electrophoretic mobilities of both were the same.

The percentage retention, $\underline{R}$, of TiO_2 in the sheet was calculated from the weights of the oven-dried and ashed sheets according to the equation in Appendix II. Approximately one-half of a sheet (1.25 g) was cut into strips and dried at 105°C for 4 or more hours. The oven-dried weight was recorded and the samples were ashed at 800°C for one hour in covered crucibles and reweighed. Agreement of duplicate results was good with differences of 3% or less in the values of $\underline{R}$.

Tensile strengths of the handsheets were measured on 5 specimens from 3 different handsheets of the same set and averaged. Reproducibility was good. The values were obtained on an Instron tensile tester at a jaw separation rate of 1 inch/min. The span was 7 inches and the width of the specimen was 1 inch. The basis weight of the sheets was about 60 g/m^2.

The optical properties of the handsheets were measured on a General Electric Recording Spectrophotometer (GERS) at 650 nm and on a Bausch & Lomb Opacimeter. On the former instrument the values of $\underline{R}_o$ and $\underline{R}_\infty$, the reflectances of a sheet of paper when backed by a black body and of a pad of paper of sufficient thickness to be opaque, respectively, are measured.

Determinations on 6 specimens taken from various locations in 2 sheets from the same set are averaged. The reflectances together with the basis weight are converted into the specific scattering coefficient s with the aid of a computer program based on the Kubelka-Munk equation (16, 17). The parameter s is a direct measure of the ability of the paper sample to scatter light. The TAPPI opacity was measured in accordance with TAPPI Method T 425 m-60. Neither the reflectances nor the TAPPI opacity showed a difference in properties of the wire side compared with the top side.

RESULTS AND CONCLUSIONS

The results for fifty sets of handsheets prepared with various additives will be considered in this report. The kinds and amounts of additives, the percentage retention of TiO_2, zeta potential of the white water, specific scattering coefficient, TAPPI opacity, and tensile strength are presented in Table II. For comparison with mill conditions, it is pointed out that 10 mg additive/40 g pulp is equivalent to 1/2 lb/ton. The variation of these properties with each other for all the sets will be discussed first, followed by detailed considerations of the effects of the various additives.

Set 1 was a control sample containing no TiO_2 or additives. It established a base line for tensile strength and optical properties and was used to determine the contribution of the pulp in the ashing procedure for the TiO_2 retention determination. Set 2 consisted of pulp and 5% TiO_2 with no additives. The retention of the TiO_2 by the pulp, both negatively charged, probably occurs by a mechanical sieving mechanism only which accounts for the low value (5%). The succeeding sets were comprised of pulp, TiO_2, and various additives as retention aids.

All of the sets but three showed enhanced retention over that with no additives. These three (Sets 17, 19, 20) were cases where a large excess of cationic polyelectrolyte was added, causing both the TiO_2 particles and fibers to acquire a positive charge. The mutual repulsion of these charges vitiated coflocculation. The formation of all the handsheets was good indicating that even with high retention no premature flocculation of the fibers occurred.

TABLE II

HANDSHEET PROPERTIES

Set No.	Additive Type	Additive Amount, mg/40 g pulp	ζ, mv	R, %	Tensile Strength, kg/cm	s, cm^2/g	TAPPI Opacity
1	—— no TiO_2 ——		-25	0	2.13	344	76.5
2	none		-21	5	2.17	372	79.5
3	PEI[a]	50	-25	73	1.94	559	87.0
4	PEI[b]	50	-25	68	1.97	540	87.2
5	PEI	50	-22	71	2.03	546	87.4
6	PEI V-500	50 10	-20	71	1.98	557	87.7
7	PEI	100	-24	65	2.03	530	86.6
8	PEI V-500	100 10	-26	59	1.97	507	85.8
9	PEI	200	-23	57	2.12	512	86.4
10	PEI	400	12	46	2.22	481	85.5
11	PEI	500	+8	28	2.17	439	83.3
12	PEI	600	+6	29	2.22	441	83.0
13	PEI	750	+9	25	2.28	423	82.6
14	PEI V-500	750 25	+9	26	2.38	424	82.9
15	PEI V-500	750 50	+7	33	2.47	434	83.2
16	PEI V-500	750 100	+7	32	2.59	433	82.9
17	Tydex	500	+20	3	2.67	354	80.0
18	Tydex	250	-8	32	2.45	433	83.4
19	Tydex	500	+22	3	2.54	353	79.0
20	Tydex	375	+22	4	2.56	359	79.8
21	Tydex	310	+20	9	2.54	373	80.2
22	Tydex	250	-12	32	2.38	435	83.6
23	Tydex V-500	310 67	-18	41	2.43	445	84.4
24	Tydex V-500	310 33	+15	25	2.62	407	83.7

See end of table for footnote.

TABLE II (Continued)

HANDSHEET PROPERTIES

Set No.	Additive Type	Additive Amount, mg/40 g pulp	ζ, mv	R, %	Tensile Strength, kg/cm	s, cm^2/g	TAPPI Opacity
25	Tydex V-500	310 50	+5	33	2.52	439	84.4
26	Tydex V-700	310 50	+14	24	2.71	407	83.0
27	Tydex V-700	310 67	-12	34	2.52	430	83.8
28	Tydex V-700	310 60	-13	31	2.47	426	83.4
29	Tydex V-70	310 67	-13	30	2.54	427	83.7
30	Tydex V-70	310 50	+5	17	2.70	391	81.4
31	Reten 300	48	-27	44	2.13	440	82.4
32	Reten 300	97	-19	53	2.12	403	80.9
33	Reten 300	19	-30	33	2.01	399	80.7
34	Reten 300	5.8	-27	9	2.14	375	79.4
35	PEI	27	-19	62	1.88	543	87.2
36	PEI	13	-20	51	1.85	514	85.6
37	PEI	6.7	-27	26	2.07	437	82.6
38	Tydex	13	-20	38	2.04	478	84.8
39	PEI[c]	50	+4	16	2.04	411	82.4
40	Tydex V-500	310 100	-22	64	2.56	491	86.2
41	Tydex V-500	310 150	-16	73	2.39	506	86.1
42	Tydex	50	-22	82	1.89	577	87.8
43	Alum	1600	-20	55	1.97	489	84.5
44	Alum	800	-19	53	1.98	490	84.9
45	Alum V-500	800 100	-22	37	2.08	433	82.0
46	Reten 300	72	-22	60	2.10	403	80.9
47	Reten 300[c]	72	+20	23	1.76	425	82.4

See end of table for footnote.

TABLE II (Continued)

HANDSHEET PROPERTIES

Set No.	Additive Type	Additive Amount, mg/40 g pulp	ζ, mv	R, %	Tensile Strength, kg/cm	s, cm^2/g	TAPPI Opacity
48	Tydex[d]	310	-8	23	2.22	401	82.7
	V-500	67					
49	Chitosan	13	-24	54	1.96	485	84.9
50	Tydex	310	-15	66	2.75	497	86.2
	V-500	200					

[a] PEI added to mixture of pulp and TiO_2.
[b] PEI added to pulp, followed by TiO_2.
[c] Polymer added to deckle box.
[d] Tydex added to TiO_2. V-500 added to deckle box.

The effect of retention on the specific scattering coefficient is shown in Fig. 10. Within the experimental scatter the data can be represented by a straight line. Exceptions are some of the sheets containing Reten 300 represented by triangles and some containing a Tydex/V-500 combination represented by squares. For these deviants the optical efficiency of the retained TiO_2 is poor, and they will be further discussed below.

The correlation of TAPPI opacity with retention is also good as shown in Fig. 11. Again the sheets that showed marked negative deviations in Fig. 10 exhibit an opacity that is somewhat below the mean. The data of Brill and Hecklau (18) on the retention of TiO_2 also fit the smooth curve very well.

The data for the tensile strength plotted against retention in Fig. 12 show considerably greater scatter. This is partly a result of the reduced precision of the tensile strength measurement compared with the optical measurements. A more important factor is that the tensile strength is not only determined by the amount of TiO_2 present but also by the amounts and kinds of polymers added which can act under some conditions as dry strength agents. The general trend, as expected, is toward a decreasing tensile strength with increasing retention since the adsorbed TiO_2 decreases the area of intimate fiber contact and concomitant hydrogen bond formation.

The most surprising correlation found in the handsheet work to date is that between retention and the zeta potential of the white water. It was assumed in the early work that a zeta potential near zero would produce the greatest retention and efforts were made to adjust the polymer concentrations to achieve this value. As the retention data became available, it was apparent that this rule of thumb did not hold for our system. Improved retention was

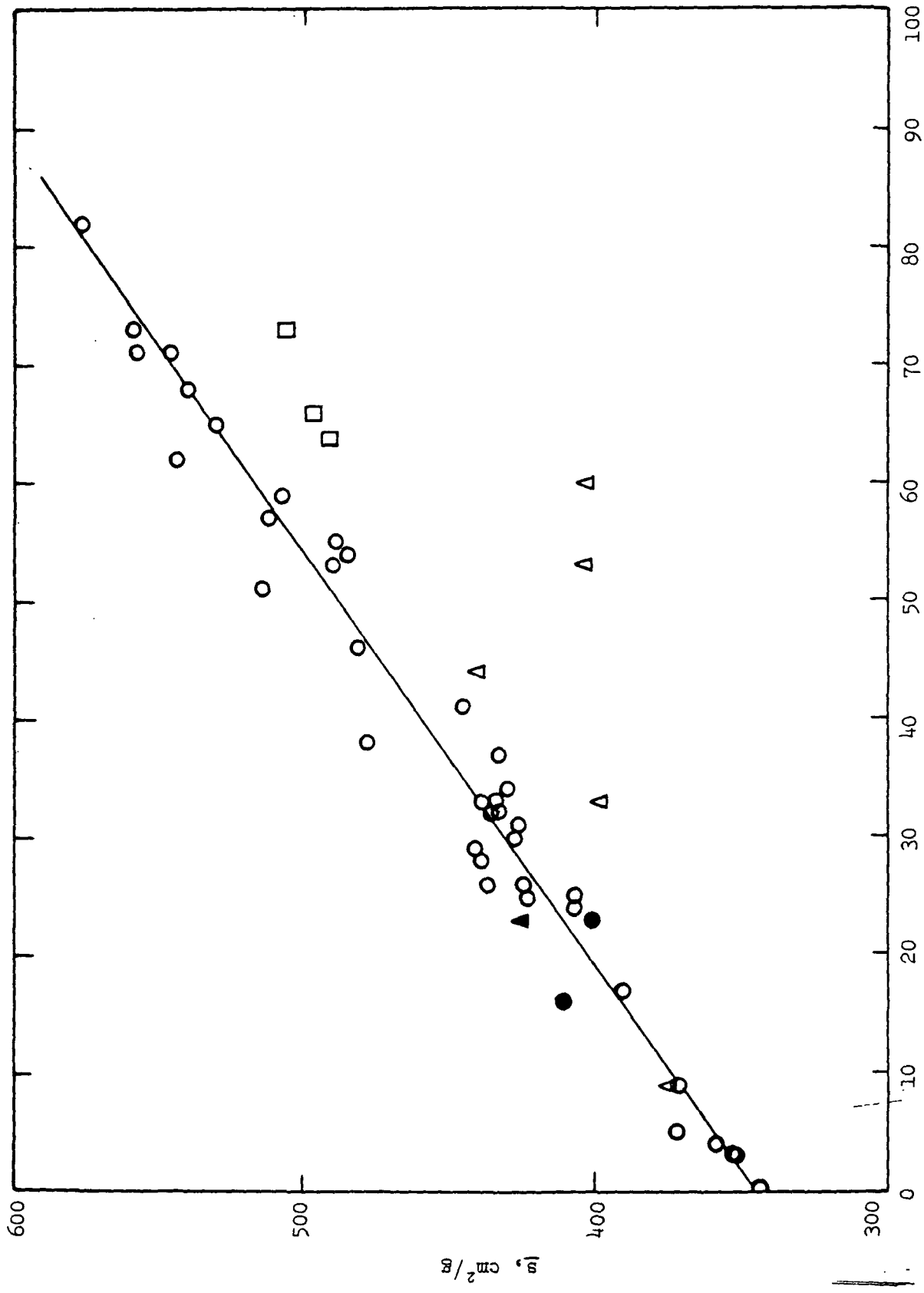


Figure 10. Specific Scattering Coefficient of Handsheets Plotted Against Retention of TiO_2. Symbols Identified in Text

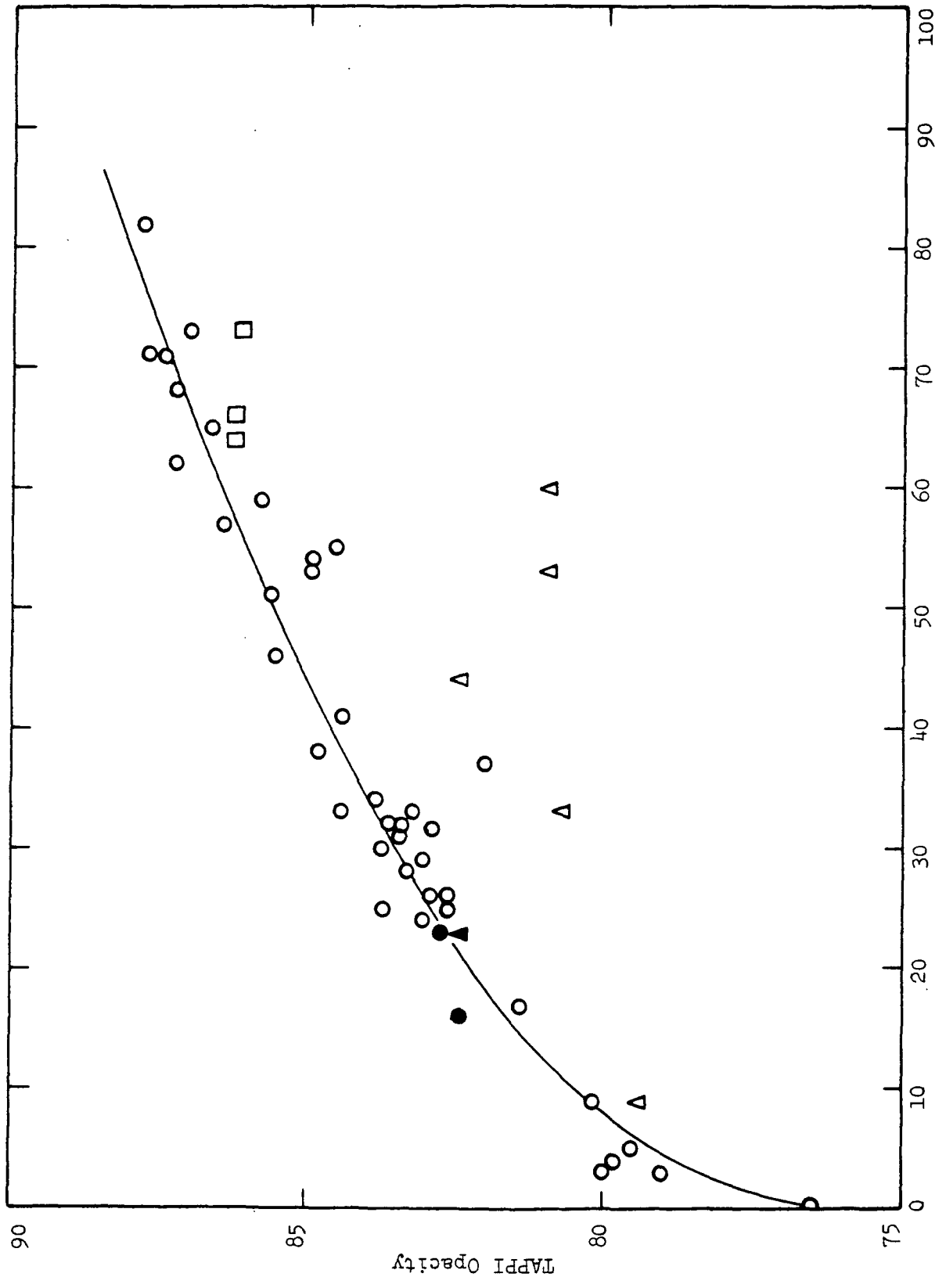


Figure 11. TAPPI Opacity of Handsheets Plotted Against Retention of TiO_2. Symbols as in Fig. 10

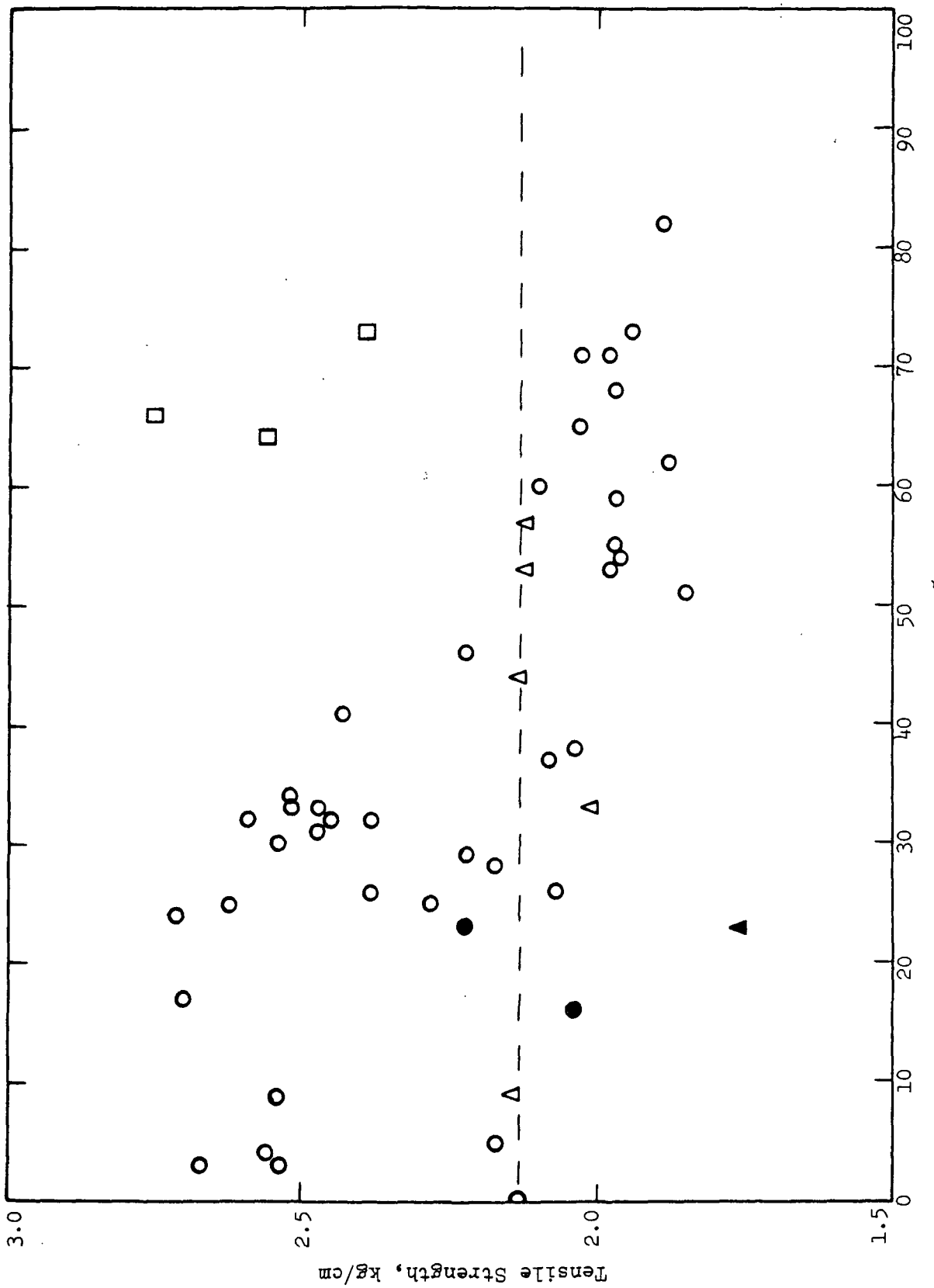


Figure 12. Tensile Strength of Handsheets Plotted Against Retention of TiO_2. Symbols as in Fig. 10. Dashed Line Indicates Strength Level with no TiO_2 or Additives

found at highly negative zeta potentials as shown in Fig. 13. At zeta potentials greater (algebraically) than about -15 mv the trend is clear; the curve drawn in at the more negative values is speculative. The conclusion to be drawn is that charge neutralization is not necessary for effective retention. Britt (19) has also found good retention of fines at relatively large negative zeta potentials. The results on TiO_2 retention are in accord with those in Part I on flocculation of TiO_2 — a net zero charge on the materials is not necessary or even desirable for maximum effectiveness. Consideration of selected systems below will illustrate this point more clearly.

EFFECT OF CONCENTRATION OF PEI (Sets 5, 7, 9-13, 35-37)

In this series the PEI was mixed with the TiO_2 prior to addition to the pulp. Only the concentration of PEI was varied. The retention and zeta potential are plotted against concentration in Fig. 14. There is an optimum concentration for maximum retention which occurs at a zeta potential of -22 mv. The shape of the retention curve and the magnitudes of the zeta potential are reminiscent of the results for the flocculation of TiO_2 by PEI in Fig. 8. Supplementary experiments on the TiO_2/PEI mixture at the optimum concentration prior to addition to the pulp showed that about 87% of the PEI remained unadsorbed and that the zeta potential was positive. Undoubtedly the excess PEI subsequently adsorbed to the pulp. Indeed it is postulated that at the higher concentrations of PEI the adsorption of the polymer onto the fibers produces local regions of high positive charge density which inhibit the adsorption of the positively charged, PEI-coated TiO_2 particles. This leads to reduced retention and eventually to positive zeta potentials. Unexplained at present is the fact that the free TiO_2 particles (as well as the fines) in the white water in the region of maximum retention have negative zeta potentials whereas before mixing with the pulp they were positive. Further work will be directed toward elucidating this behavior.

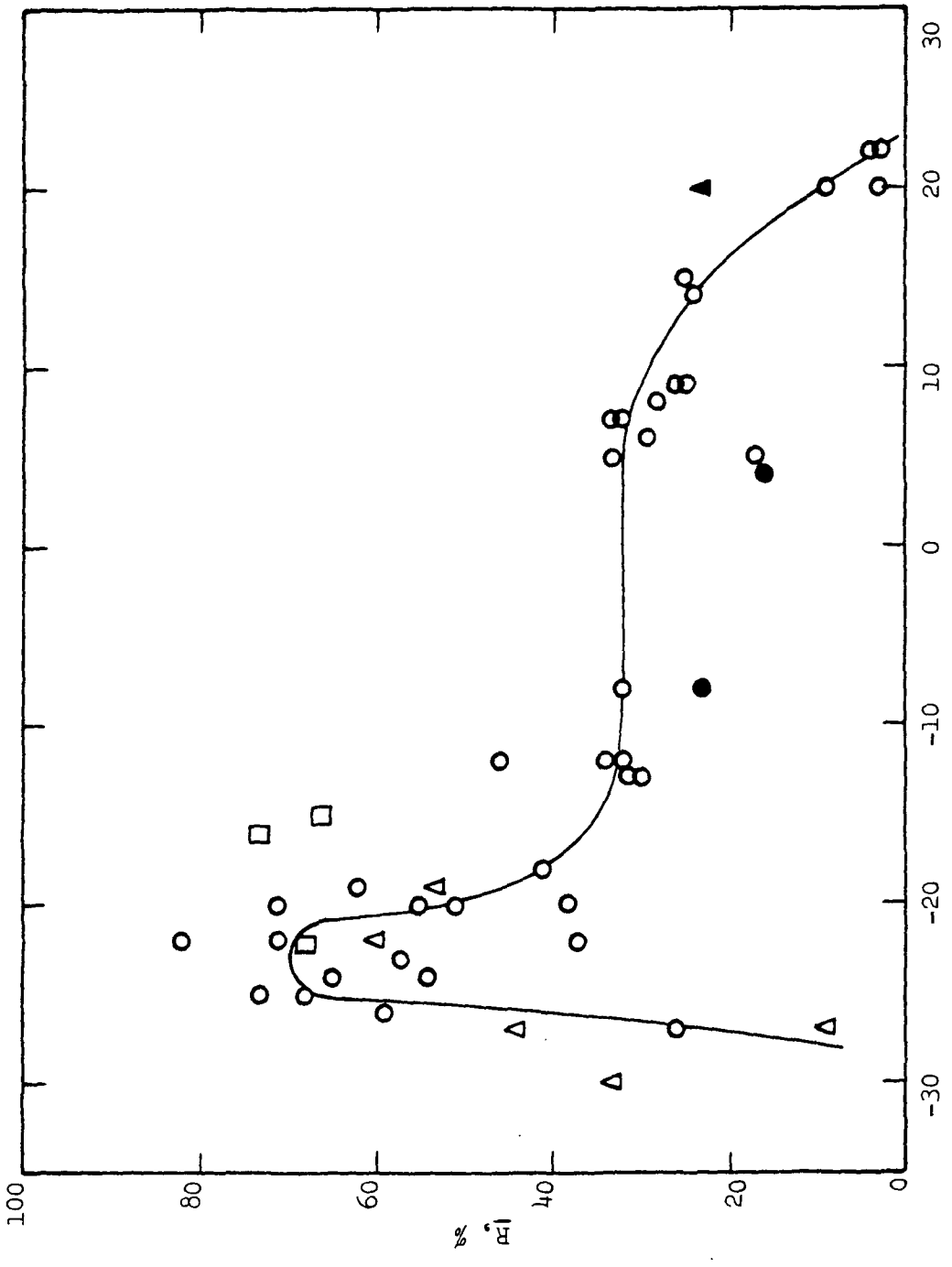


Figure 13. Retention of TiO_2 in Handsheets Plotted Against Zeta Potential. Symbols as in Fig. 10

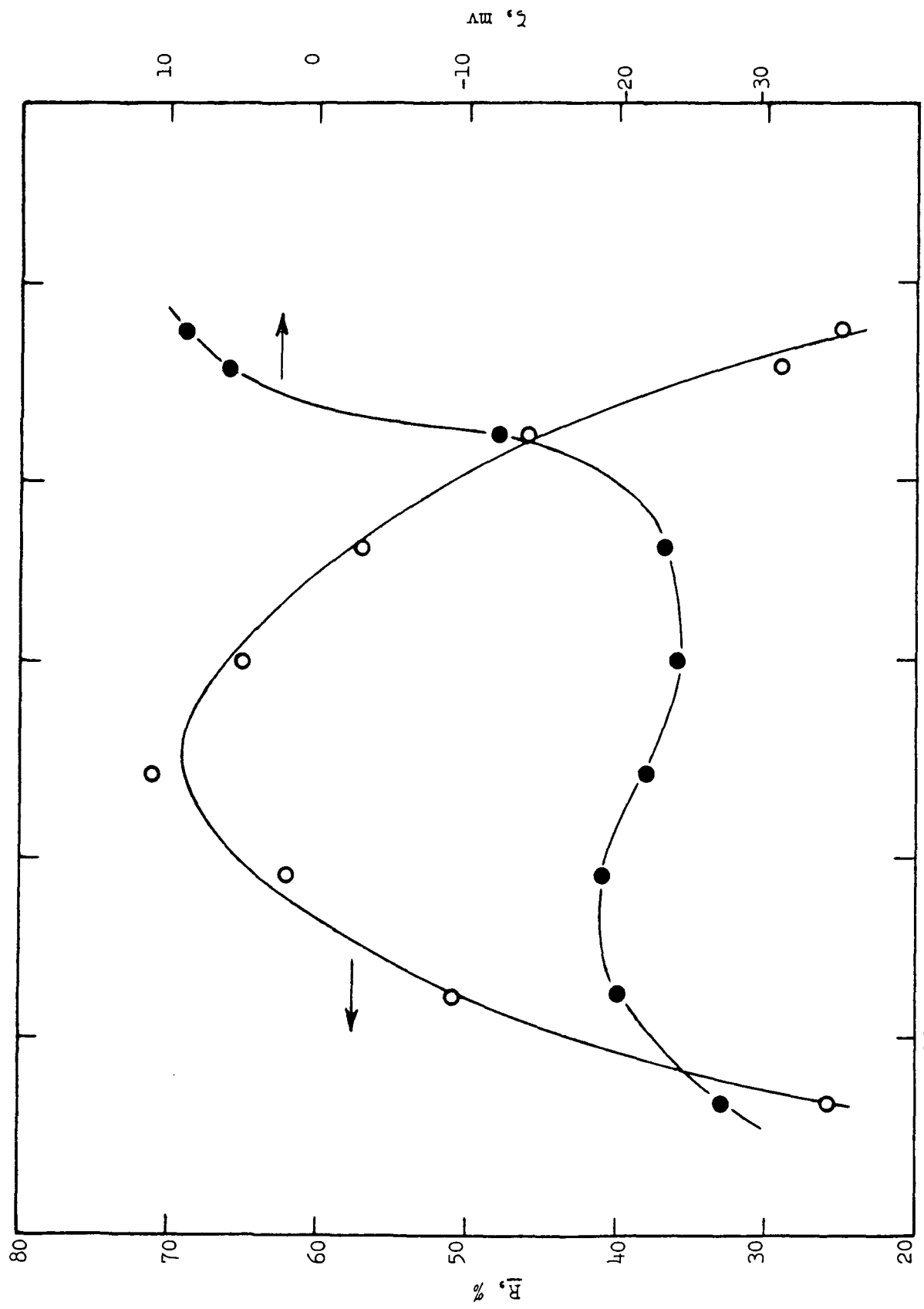


Figure 14. Retention and Zeta Potential of TiO_2 on Handsheets Plotted Against the Logarithm of the PEI Concentration

EFFECT OF CONCENTRATION OF TYDEX (Sets 17-22, 38, 42)

This series is very similar to the preceding one except the polymer has been changed. The results are very nearly the same with a maximum retention of 82% at a concentration of 50 mg PEI/40 g pulp. Apparently, the two polyethylenimine samples have quite similar capabilities in functioning as retention aids.

EFFECT OF SEQUENTIAL ADDITION OF CATIONIC AND ANIONIC POLYELECTROLYTES (Sets 23-25, 40, 41, 50)

In this series a large excess of Tydex was mixed with the TiO_2. With no additional additives, a high zeta potential (+20 mv) and a poor retention result (see Set 21). The TiO_2/Tydex dispersion was then mixed with the pulp for 2-1/2 minutes, a given concentration of NaPSS (V-500) was added, and mixing was continued for another 2-1/2 minutes before dilution and handsheet formation. The results are presented in Fig. 15. Where the V-500 molecules adsorb on the positively charged pulp and TiO_2, they create local areas of high negative charge. These become sites for coflocculation of the TiO_2 and pulp. The importance here of the LaMer bridging mechanism with its prediction of a strong dependence on molecular weight is being investigated by work in progress using V-70 and V-700 in place of V-500. In light of the flocculation studies in Part I little effect of molecular weight is expected.

Once again only modest retention is obtained at the point of charge neutralization ($\zeta = 0$). Although fairly high retention is possible, the requisite polymer addition levels are rather impractical. Furthermore, the optical efficiency is poor as can be seen in Fig. 10 where data are indicated by squares. On the other hand, considerable strength is imparted at the

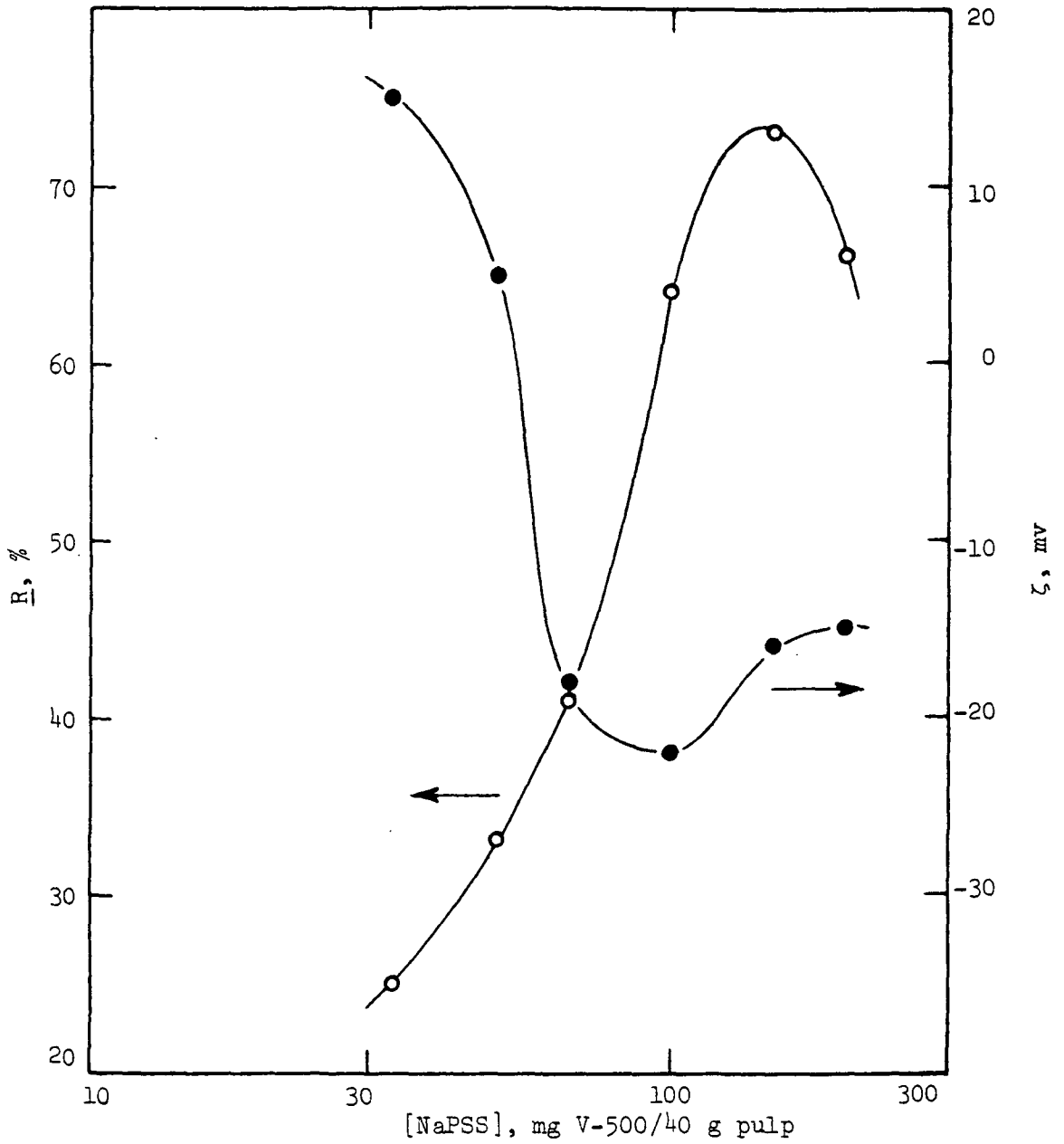


Figure 15. Retention and Zeta Potential of TiO_2 on Handsheets Plotted Against the Logarithm of the NaPSS Concentration. TiO_2 was Pretreated with 310 mg PEI/40 g Pulp

high addition levels of the dual polymer system as shown by the square data points in Fig. 12. It is probable that combinations of Tydex and V-500 both at considerably lower concentrations would also produce effective retention. The objective of the series was merely to demonstrate the efficacy of the dual polymer approach and the state of the surface charge at maximum retention.

EFFECT OF THE ORDER OF ADDITION OF COMPONENTS (Sets 3-5, 39)

Here the retention aid (PEI at a concentration of 50 mg/40 g pulp) was held constant and only the order of addition of the furnish components was varied. The combination PEI/TiO_2 was added to the pulp (Set 5), PEI was added to the pulp followed by the TiO_2 (Set 4), TiO_2 was added first to the pulp followed by PEI (Set 3), or the pulp and TiO_2 were mixed and diluted and the PEI was added at the deckle box (Set 39). Little difference was noted between the sheets produced by the first three variations. The retentions were between 67 and 73%, the zeta potentials between -22 and -25 mv, and the strength and optical properties were nearly the same. The results for addition at the deckle box are markedly different. The zeta potential here is positive (+4 mv) producing poor retention (16%). The effects of addition at the deckle box will be discussed in more detail below. It can be concluded that the order of addition of components before the deckle box is unimportant for the case of PEI used alone as the retention aid.

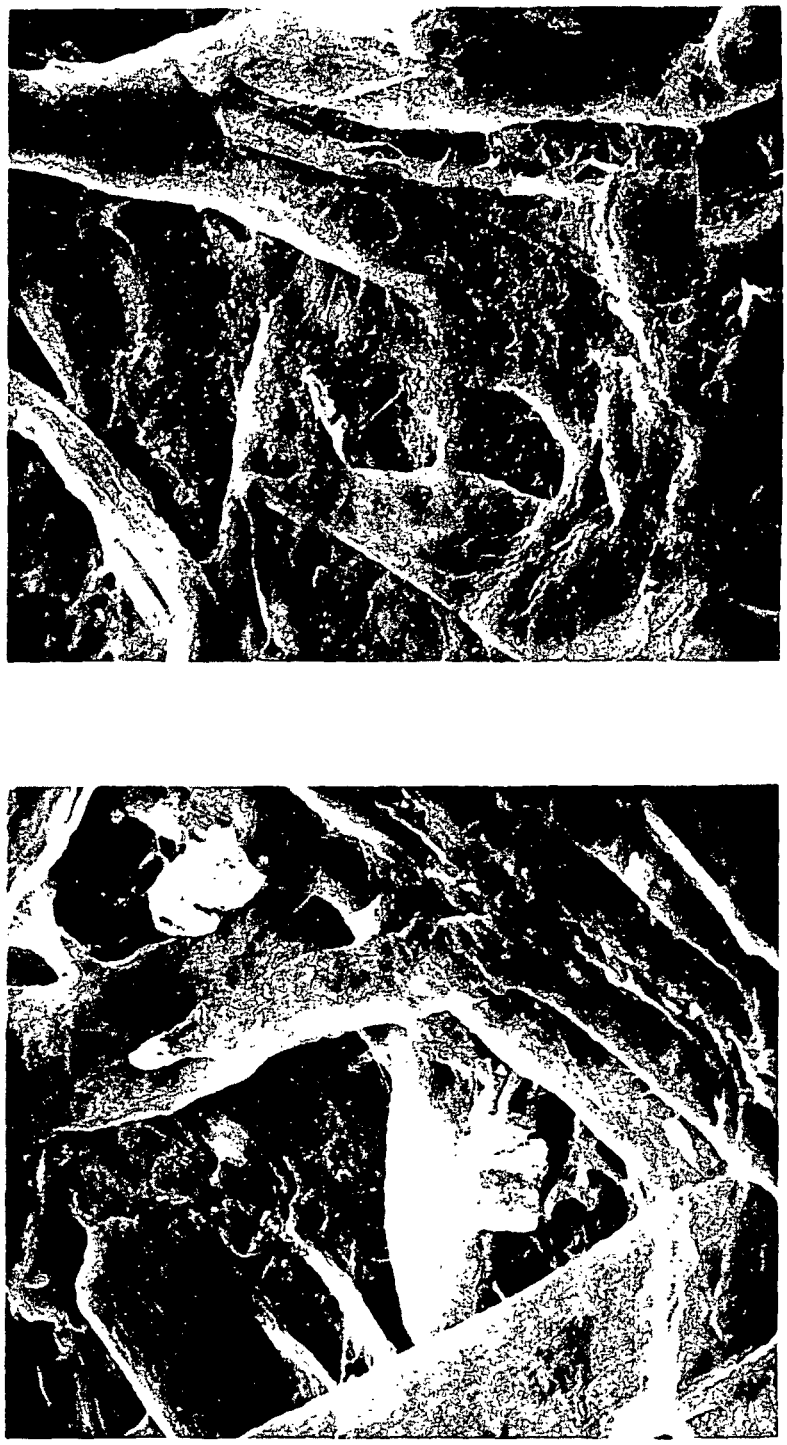
EFFECT OF RETEN 300 AS A RETENTION AID (Sets 31-34, 46)

Based on the invariance of results with order of addition just described, the Reten 300 was added directly to the TiO_2 as had been done with the other cationic polymers. This turned out to be a mistake. Reasonably good retentions (up to 60%) were obtained but the optical efficiency was deplorable as shown by the triangular data points in Fig. 10 and 11. To bear out our suspicions,

scanning electron micrographs were made of the surfaces of two handsheets. Set 32 was formed with 97 mg Reten 300/40 g pulp while Set 36 was formed from 13 mg PEI/40 g pulp. Both had retentions of about 51% and similar zeta potentials but the specific scattering coefficients were vastly different — 403 (Set 32) vs. 514 (Set 36). The photomicrographs are shown in Fig. 16. As suspected, the Reten 300 produced preflocculation of the TiO_2 as evidenced by the few large particles (about 15 μm across) with consequent poor scattering. On the other hand, the TiO_2 is distributed relatively uniformly in Set 36 mostly as individual particles. Apparently, the higher molecular weight of the Reten 300 compared to that of PEI caused flocculation of the TiO_2 to occur during addition before a high enough concentration was reached to effect restabilization. It is probable that addition to the furnish after the TiO_2 has been mixed with the pulp will lead to better optical efficiency. Such trials are in progress.

EFFECT OF ADDITION AT THE DECKLE BOX [Sets (5, 39), (46, 47), (23, 48)]

Three different series of retention aids are considered here. Sets (5, 39), (46, 47), and (23, 48) are representative of a low molecular weight cationic polymer (PEI), a medium molecular weight cationic polymer (Reten 300), and a cationic/anionic dual polymer system (Tydex/V-500), respectively. In each series the concentrations of the components are held constant. The polymer(s) for the first member of each series was added at the usual point(s). For Sets 39 and 47 the cationic polymer was added instead to the deckle box while for Set 48 the cationic polymer was added as usual and the anionic polymer was added to the deckle box. For ready comparison the pertinent data are repeated in Table III. The effects are striking.



b

a

Figure 16. Scanning Electron Micrographs of Handsheet from (a) Set 32 and (b) Set 36. Magnification: 800X

TABLE III

DATA FOR DECKLE BOX ADDITION

Set	ζ, mv	R, %
5	-22	71
39	+4	16
46	-22	61
47	+20	23
23	-18	41
48	-8	23

The zeta potentials for the sheets with deckle box addition are more positive than their counterparts and the retentions are correspondingly lower. The data indicated by the black symbols in Fig. 13 do not follow the general trend of the handsheets formed in the "normal" manner.

No simple explanation can be given at present for this behavior. The only obvious difference in conditions is that the consistency in the deckle box is about 0.04% while at the point of usual addition of pigment and polymer it is 1.5%. In unreported experiments, increasing the length of time in the deckle box to one minute along with continuous gentle agitation produced no change in white water zeta potential and only slight improvement in retention. Hence, the effect is not just a function of contact time. It is expected that experiments in progress concerning the changes in zeta potential during the several steps in furnish preparation will provide an explanation for the differences found.

EFFECT OF CHITOSAN (Set 49)

Although only one set of handsheets has been formed using this retention aid, it would appear to merit further study. At the relatively low

addition level of 13 mg/40 g pulp the retention was 54% compared with retentions of 50% and 38% for PEI and Tydex at this level. Work is in progress to determine the optimum concentration for maximum retention.

GENERAL CONCLUSIONS

The conclusions that can be drawn from the data in hand are that high retention can be achieved with either single (cationic) or dual (cationic/anionic) polymer additives. The colloidal conditions for maximum retention are not those of complete charge neutralization ($\zeta = 0$). Rather, a fairly large, negative zeta potential (-18 to -26 mv) is found for the best results.

FUTURE WORK

Studies on the retention of TiO_2 on handsheets will be extended to systems with electrolytes present to more closely simulate mill conditions. Once this groundwork is laid, emphasis will be shifted toward ascertaining the effects of high-speed drainage on retention using the dynamic drainage tester (20).

Experiments are in progress to determine the effects of controlled amounts of shearing on floc stability under laminar flow conditions. These investigations will subsequently be extended into the turbulent regime.

At a later date the studies will be directed toward obtaining an understanding of the factors important to the retention of fines with the aid of polyelectrolytes. Machine conditions will be approximated by sheet formation on handsheet molds and on the dynamic drainage tester.

ACKNOWLEDGMENTS

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APPENDIX I

CALCULATIONS BASED ON THE LANGMUIR ADSORPTION ISOTHERM

The equation for Langmuir-type adsorption (21) can be written

$$\Gamma = \Gamma_M K C_e/(1 + K C_e) \qquad (2)$$

where Γ is the specific adsorption in units of mg polymer per g TiO_2, Γ_M is the maximum amount of polymer per g of TiO_2 that can be adsorbed as the equilibrium polymer concentration C_e goes to infinity, and K is the Langmuir affinity constant. It is convenient to multiply Equation (2) by C_τ, the number of g of TiO_2 per liter of suspension. The results can be written

$$C^* = C_M^* K C_e/(1 + K C_e) \qquad (3)$$

where C^* is the mg/liter of polymer that has adsorbed on the TiO_2 and C_M^* is the maximum this quantity can reach. The parameters C^* and C_M^* are functions of the amount of TiO_2 present whereas Γ and Γ_M are not. Equation (3) can be rearranged to give the following

$$C_e/C^* = (K C_M^*)^{-1} + C_e/C_M^* \qquad (4)$$

Equation (4) predicts a linear relationship between C_e/C^* and C_e with a slope of $(C_M^*)^{-1}$ and an intercept of $(K C_M^*)^{-1}$. Figure 3 shows such a plot and Table I presents the derived constants.

Once the constants C_M^* and K have been determined for a given system it may be of interest to know the amount of polymer adsorbed starting with an arbitrary initial concentration C_i. Since C_e and C^* must sum to C_i, Equation (3) can be rewritten as

$$C^* = K C_M^* (C_i - C^*)/[1 + K (C_i - C^*)] \qquad (5)$$

This equation is quadratic in $\underline{C}^*$ and may be solved to give

$$C^* = B - (B^2 - C_M^* C_i)^{1/2} \tag{6}$$

where

$$B = 1/2\ [(K)^{-1} + C_i + C_M^*]. \tag{7}$$

Alternatively, the fraction $\theta = \underline{C}^*/\underline{C_M^*}$ may be the quantity sought when given an initial concentration $\underline{C_i}$. The solution in this case is

$$\theta = (B/C_M^*) - [(B/C_M^*)^2 - (C_i/C_M^*)]^{1/2} \tag{8}$$

with $\underline{B}$ given by Equation (7). The quantity θ may be thought of (roughly) as the fraction of the surface covered with polymer.

One other calculation which is the inverse of that just preceding answers the question: what must the initial concentration of polymer be to attain a given fractional surface coverage? Equation (5) can be solved for $\underline{C_i}$ and written in terms of θ.

$$C_i = [\theta/K\ (1 - \theta)] + C_M^*\ \theta\ . \tag{9}$$

A sample calculation is given here for the case of optimum flocculation of 1000 mg/liter TiO_2 by PEI at a pH of 5. We are interested in calculating the fractional surface coverage at this concentration. From Table I the Langmuir constants are 15.6 and 1.6 for $\underline{C_M^*}$ and $\underline{K}$, respectively. The value of $\underline{C_M^*}$ is that corresponding to 7400 mg/liter and must be corrected to the sample in question by multiplying by the ratio (1000/7400). This value (2.11) of $\underline{C_M^*}$ and that for $\underline{K}$ (which remains unchanged) may be substituted into Equations (7) and (8) to yield a θ of 0.090.

APPENDIX II

CALCULATION OF PERCENTAGE RETENTION

The percentage retention, $\underline{R}$, of TiO_2 in a handsheet was calculated from the ovendry weight of the sheet $\underline{W_o}$, the ash weight $\underline{W_A}$, and the ratio $\underline{f}$ of the ash weight to ovendry weight of a sheet with no TiO_2 in it. The following simultaneous equations can be written.

$$W_o = W_p + W_t \tag{10}$$

$$W_A = fW_p + W_t. \tag{11}$$

The two unknowns are the ovendry weights of pulp and TiO_2 in the sheet, $\underline{W_p}$ and $\underline{W_t}$, respectively. From the ovendry and ash weights of handsheet Set No. 1 (pulp only) the fraction $\underline{f}$ was found to be 0.0034. The ash weight of the TiO_2 by itself was negligibly different (99.9%) from its ovendry weight.

The two equations are solved to give

$$W_t = W_A - 0.0034\ (W_o - W_A) \tag{12}$$

and

$$W_p = W_o - W_t. \tag{13}$$

Since the TiO_2 to be added is weighed out at 5% on the weight of the ovendried pulp in the furnish, the percentage retention can be given by

$$R = 100\ W_t/0.05\ W_p = 2000\ W_t/W_p \tag{14}$$

with $\underline{W_t}$ and $\underline{W_p}$ given by Equations (12) and (13). It is assumed in this calculation that polymers or other additives contribute negligibly to $\underline{W_o}$ and $\underline{W_A}$.

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